Preparation of Graphene from Graphene oxide by Chemical Reducing Agents

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Abstract

Graphene, an atomically sp^2 hybridized thin two-dimensional carbon community material, got prodigious attention in the scientific field. Particularly, this review aims to provide the preparation approaches which can be used to reduce the oxygen assembly of graphene oxide to graphene. This review provides literature on the chemical reducing agents up to 2020.

Keywords: Graphene, Graphene oxide, Chemical methods, reducing agents.

Introduction

Graphene, a two-dimensional nanomaterial consisting of monolayer sp^2 assembled carbon community. Graphene as a rising star has the mass invention of graphene is of inordinate interest for commercialization and industrial applications. Reducing chemically the Graphene oxide (GO) is solitary of conservative approaches to build graphene production to a large scale.

Just like graphite, graphene is connected with stacked layers with van der Waals forces and possesses unique properties depending on the selected production methods. To attain the graphene by the conversion of GO, various novel synthesis methods are envisaged. Firstly, Novoselov and Geim have reported achieving the graphene similar to pristine graphene, from bulk graphite by mechanical exfoliation with the help of scotch tape[1]. Further, several methods have been reported for graphene, mainly classified into approaches[2] such as bottom-up and top-down. Mainly, bottom-up approaches are chemical vapor deposition - CVD[3], arc discharge[4], epitaxial growth on SiC[5], CO reduction[6], CNTs unzipping[7], etc. methods are used for the production of graphene directly from graphite derivatives. Where in, top-down approaches primarily comprise: micromechanical exfoliation[1], thermal exfoliation[8], solvent-exfoliation[9], and chemical reduction of GO[10].

In the production technique of graphene, firstly, graphite is subjected to oxidation and exfoliation into GO layers by reactive oxidizing reagents and then followed by the reduction with reducing agents at the specific reaction temperature, that produces graphene with the deoxygenating effect of GO, as HRG- highly reduced graphene oxide or CMG- chemically modified graphene, or CRG- chemically reduced graphene of RGO- reduced graphene oxide nanosheets.

These nanosheets generally are named graphene as per the literature. The transformation of GO to graphene by investigation, specified by the colour variation from brown colour GO suspension to black colour graphene and enlarges the surface area with hydrophobicity or aggregation of the graphene sheets which emit with the removal of oxygen functionalities.

Despite the wide range of strategies for graphene production, solution-based or wet chemical synthesis (top-down approach) is more suitable for the industrial level synthesis of graphene. The "top-down" approach is auspicious to accomplish the synthesis of low-cost large-scale graphene. This approach is a simple, efficient strategy of natural graphite oxidation by strong agents for oxidization to GO. Moreover, it has low-cost with a bulk amount of graphene like sheets conventional and can be fabricated into a variety of materials. The usual approaches comprise graphite micromechanical exfoliation[1], liquid-phase exfoliation of graphite[11], & the most well received wet chemistry method *via* an intermediate of graphene oxide. The GO reduction can be attained through chemical reducing agents[12], photos as well as thermal reduction[13], & bacterial reduction[14].

Synthesis of graphene by solution based/wet chemical method

The large-scale production of graphene is mainly done by the wet chemical reduction method. It means, firstly, the conversion of GO from pristine graphite using strong oxidizing agents, and exfoliation to GO layers and then reduction to graphene, using various chemical reducing agents and/or physical, biological, hydrothermal, thermal/microwave irradiation, green and eco-friendly reduction methods are used for the synthesis of graphene.

In these processes, GO contain sp^3 hybridized carbon skeleton into sp^2 hybridized carbons with the regeneration of conjugated skeleton in graphene. Chemically modified graphene usually termed RGO- reduced graphene oxide is the graphene obtained by this method. In reduced graphene oxide-RGO, every sp^3 hybridized carbons aren't reconverted to sp^2 hybridized carbons by oxygen-comprising functional groups which will retain on RGO. As a result, RGO's extended π-conjugation differs from those of pure graphene, and its electrical conductivity is significantly lower to pure graphene. RGO's electrical and chemical properties are also affected by reaction conditions such as temperature, duration, and the amount of oxidizing & reducing agents used. Despite the concept that RGO differs from pure graphene, it is frequently referred to as graphene mostly in literature. Overall, this review is mainly focused on the chemical reduction of GO by chemical reducing agents like hetero atom containing like N, O, S, Al, B, halides, metal-acid and metal-basic medium, etc. We discussed some of the major literature reports on the synthesis of graphene, starting with an attempt to introduce graphene as a building block from various chemical reducing agents for high-quality graphene nanosheets can be produced on large scale.

Chemical reduction of graphene

Different chemical reduction methods are used to prepare graphene. In these methods, the prepared graphene is oxidized to graphene oxide (GO). Various chemical reducing agents like hetero atom containing N, O, S, Al, B, halides, metal-acid and metal-basic medium, etc. are used to achieve a solution-based reduction in exfoliated GO dispersions.

Synthesis of graphene using Nitrogen-containing reducing agents
Hydrazine as reducing agent

Hydrazine (N_2H_4) is generally identified for acting hydrazone with carbonyl compounds. It is significant in organic reactions like the preparation of heterocyclic compounds and wolf-Kishner reduction. Hydrazine, a general antioxidant that scavenges oxygen whereas it is cleaved to nitrogen and water. Despite the wide range of hydrazine used in industries, it is dangerous and very noxious in nature.

The formation of conjugated carbon atoms on individual graphene sheets is first conformed by Ruoff and co-workers[15] by reduced GO on treatment with hydrazine. Hydrazine is toxic, during the reduction process some C-N groups are incorporated into the sample.

The typical procedure of graphene briefly, 100 mg graphitic oxide with 100 mL water is sonicated until getting clear brown-yellow dispersion. Then 1 mL hydrazine hydrate is added & is refluxed in 100 ^{o}C oil bath for 24 h. After that, the colour changes to black from brownish-yellow, indicating the primary clue for graphene sheets formation. Later the graphene sheets were isolated by filtration and were vacuum dried. From the elemental analysis, the prepared reduced graphene was increased in atomic (C/O) ratio of 10.3 of carbon to oxygen than GO (2.7) besides 2420 Sm^{-1} electrical conductivity. By removing the oxygen functionalities, the resulting graphene shows highly hydrophobic and contains agglomeration between graphene layers. But the graphene showed lower content of oxygen and traces amount of nitrogen were exposed on graphene per a C/N ratio 16:1. Nonetheless, this approach is an important finding that can be used to produce graphene on a huge scale.

In continuation to the same group, proposed a reduction process for epoxide groups in GO[16]. Primarily, the epoxide group with a nucleophilic attack of hydrazine results in a hydrazine alcohol group with the releasing of water molecule to form aminoaziridine and to form a double bond with loss of diimide on heating. While using the hydrazine, the H-abstraction of the epoxide group gets opened to the epoxide ring is calculated by density functional theory (DFT)[16]. Further, the remaining nitrogen atoms were described for the probable creation of hydrazides and hydrazones from lactones and quinones found on GO.

On continuity for production of graphene, individual GO sheets were produced agglomeration of exfoliated sheets with larger surface area with hydrazine and no reduction was observed in not exfoliated GO sheets[17].

Follow the similar procedure, utilized with hydrazine hydrate at different temperatures for graphene[18]. The resultant graphene showed with C/O ratio 15.1 at 95 ^{o}C for 3 h and electrical conductivity 5 Sm^{-1}. Further, the isotopic ^{13}C and ^{15}N labeled graphene by the reaction between ^{13}C labeled GO and ^{15}N labeled hydrazine[19]. This resultant graphene suggests that the N$_2$ moieties in five-membered rings like pyrazole or pyrazoline ring are on the boundaries of the graphene planes. Generally, chemical substitution occurs at the boundaries on the graphene sheets, mostly diketone moiety was abundant. Further, the mechanism of the reaction was measured by Nagase along with co-workers through DFT calculations[13].

On another note, using hydrazine hydrate in both aqueous[20] and organic[21] medium to produce colloidal suspensions of grapheme were available. Moreover, graphene was obtained from reduction GO with hydrazine hydrate to develop graphene-based sensors[22,23], antioxidant activity[24], Fuel cells[25], supercapacitors[26], etc.

Phenylhydrazine as a reducing agent

Chung and co-workers[27] reported that GO is reduced with phenylhydrazine which has stable dispersions in several polar aprotic organic solvents like N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMAc), propylene carbonate (PC), and also 1-methyl-2-pyrrolidinone (NMP). Resulting graphene is unwavering, due to which is covalently bonded with phenylhydrazine is maintained steric effects, in that way which preventing aggregation of graphene sheets and showed an electrical conductivity as 20950 Sm^{-1}.

Hydroxylamine as reducing agent

Guo and co-workers[28] reported a rapid approach to GO reduction employing the reducing agent hydroxylamine under mild conditions. In this experiment, hydroxylamine can be obtained from hydroxylamine hydrochloride (NH$_2$OH.HCl) & ammonia. The obtained graphene generated a 9.7 C/O ratio and 1122 Sm^{-1} electrical conductivity at 1 h reaction conditions. The epoxide and hydroxyl groups reduction from GO by hydroxylamine molecule might attack the epoxide carbon atom and opening of epoxide to hydroxyl group with one H-atom transfer. By loss of a single water molecule to form N-hydroxylaziridine made as an intermediate and also the hydroxylamine molecule may attack β-carbon of the hydroxyl groups in GO and the transfer of a proton to the hydroxyl group to release water molecule to form similar N-hydroxylaziridine intermediate converted as a conjugated vinyl group and discharge unstable nitrogen oxide (NO$_X$) species

and a water molecule (H_2O). This mechanism is helpful in eliminating epoxide and hydroxyl groups from GO which is shown in **Fig. 1**.

Further, a one-step approach for single-layer graphene suspension using hydroxylamine hydrochloride stirred at 80 $^{\circ}$C at 30 h. The resultant graphene significantly increased C/O with 2.5 and exhibited field-effective transistor gas sensors[29].
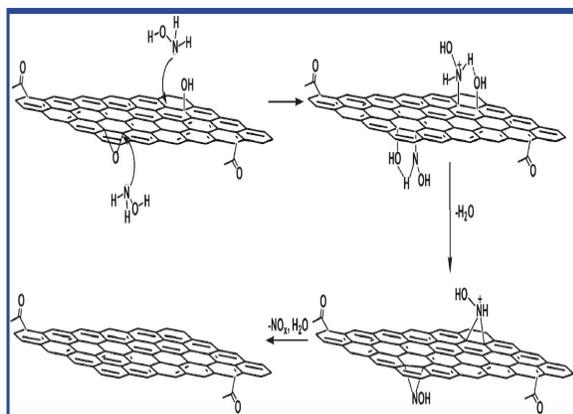

Fig. 1. The proposed mechanism in reducing GO with hydroxylamine[28].

Benzylamine as reducing agent

Sun and co-workers[30] applied benzylamine reagent for reduction, which acts as a reducing agent for GO and stabilizer for the obtained graphene. In this method GO is mixed to benzylamine for about 1.5 h, resultant graphene resulted in C/O ratio 4.7 and, 2h reaction condition it improved C/O ratio to10.2. Moreover, RGO exhibited a resistance with a measure of 5×10^8 Ω also a better stable dispersion in the aqueous phase.

The existence of polar amine groups in benzylamine molecules and even a negatively charged carboxyl group top graphene helped to preserve this stability. Then after, silver nanoparticles (Ag NPs) were added to the graphene to display high sensitivity and for electrochemical reduction of H_2O_2 detection. **Fig. 2** illustrates the production of graphene from GO using benzylamine like a reducing & stabilising agent, as well as the ensuing preparation of AgNP/graphene hybrids.
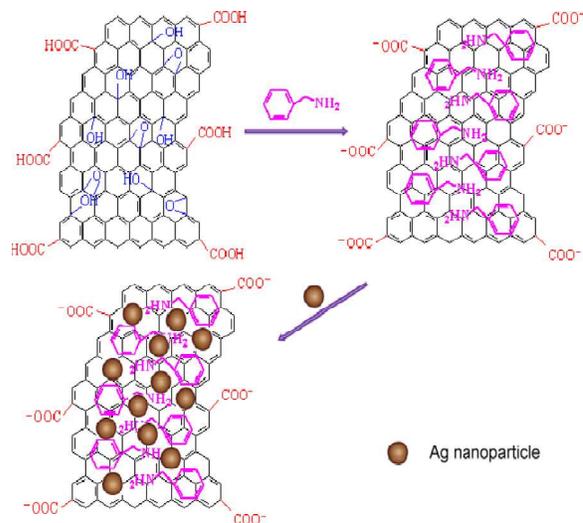

Fig. 2. Illustration of graphene formation from GO by using benzylamine as reducing & stabilizing agent and ensuing preparation of AgNP/graphene hybrids[30].

Pyrrole[31] is generally known as a weak base and a pioneer in the synthesis of many natural products. Firstly, Lee and co-workers[32] demonstrated the pyrrole as a reducing agent and stabilizing agent. It showed 7.7 C/O ratio also exhibits superior dispersion stabilities in several organic solvents like DMSO, ethanol, THF, DMF, NMP, and acetone.

Ma and co-workers[33] reported a new reduction method for graphene using *p*-phenylenediamine (PPD), which acts as a reducing and also stabilizing agent. The resultant graphene was positively charged with the adsorbed oxidized PPDs, and contained -N^+ residuals. This prohibited π–π stacking contacts and agglomeration among the graphene sheets. As such, the graphene exhibited improved dispersion stabilities in ethanol, glycol, and NMP. Further, the graphene gave a measured conductivity of 15000 Sm^{-1} in the plane of the graphene film.

Hexamethylene tetramine (HMTA)[34], a cage-like heterocyclic compound, to promote the reduction of graphene oxide. As a consequence of electrostatic stabilization of negatively charged carboxyl groups plus positively charged bound HMTA molecules, the produced graphene demonstrated good dispersion stability in an aqueous solution.

Zhao and co-workers[35] reported graphene by urea as a reducing agent. Urea in basic medium showed the good dispersion stabilities within ethylene glycol, water, and DMF for 36 h. The resultant graphene showed 4.5 C/O ratios and 43 Sm^{-1} of electrical conductivity. Further, by the urea as reducing agents to produce graphene with X-band electromagnetic absorption properties[36], adsorptions of organic dyes[37], conducting films[38], etc. and also dimethyl ketoxime[34], ethylenediamine[39], etc. reagents are also used for reduction for GO.

Synthesis of graphene using borohydrides as a reducing agent
Sodiumborohydride (NaBH$_4$)

Through organic synthesis, sodium borohydride (NaBH$_4$) is a well-known reducing agent for reducing carbonyl functional groups. The treatment of NaBH$_4$ as a reductant for the reduction of GO was initially stated by Kamat & Co-workers[40] in the preparation of gold nanoparticles physisorption on graphene sheets. In the meantime, Samulski[41] prepared GO reduction with NaBH$_4$ as the first among three-step synthesis (remove of oxygen functionalities in GO to achieve preproduction of graphene, sulphonated graphene, and post-reduction with hydrazine) towards complete reduction effort to acquire suphonated graphene, having good dispersions with water through different concentrations. The sulphonated graphene exhibited a 17 Sm^{-1} conductivity. In addition to the related reduction process with NaBH$_4$ was reported by Ajayan and co-workers[42] in their observations correlated to the total reduction of GO. Subsequently, Lee and co-workers[43] supervised the utility of NaBH$_4$ concentration on graphene with electrical properties of the developed. At 150 Mm of NaBH$_4$ concentrations with the reduction GO to graphene C/O ratio 8.6 and the conductivity is 45 Sm^{-1}.

Further, Pumera and co-workers[44] were carried out on reductant efficiency of borohydrides like sodium borohydride (NaBH$_4$), (sodium cyanoborohydride [NaBH$_3$CN] and sodium triacetoxyborohydride [NaBH$_3$(OAc)$_3$] used to effort the adopt of oxygen moieties on GO to graphene displayed variable ratios of C/O in the ranges ~2.2 to 2.5. and subsequently, the electrochemical behavior of graphene with NaBH$_4$, NaBH$_3$CN, and NaBH$_3$(OAc)$_3$ charge transfer resistances (R$_{ct}$) at 1.64, 1.72, and 4.92 kΩ compared with R$_{ct}$ of GO 2.27 kΩ.

Recently, Chung and co-workers[45] introduced ammonia borane (AB) as an effective agent for the reduction of GO in both aqueous and organic solvents (THF) to graphene. The reduction possibilities of GO with aqueous and organic solvents with ammonia borane (AB) were shown in **Fig. 3**. Ammonia borane is a mild reductant similar to NaBH$_4$ and exhibits this material as suitable for hydrogen storage. Thus, results obtained from graphene, doping with slight amounts of boron (BC$_0$), and nitrogen (pyrrolic N) were covalently bonded with graphene's carbon skeleton. Because the C/B & C/N ratios with in organic solvent reaction were lower than the aqueous solution reaction, this suggests that GO reduction in THF (organic solvent) is more effective in boron & nitrogen doping than in water (aqueous solution). Further, the graphene showed specific capacitance in the range of 100-130 G g^{-1}.
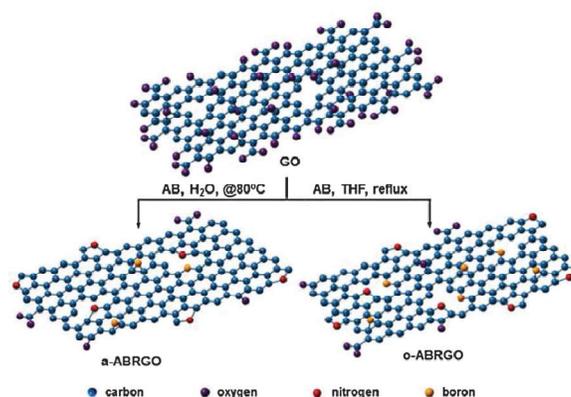

Fig. 3. The schematic sketch of GO reduction dispersed with ammonia borane (AB) in water (a-ABRO) and in THF (o-ABRO) [45].

Grace and co-workers[46] have also used for the chemical reduction of GO using NaBH$_4$ with different concentrations [1(GO):10(NaBH$_4$)]. The electrical conductivity of graphene sheets are high with increased to 208.5 S/m than GO (0.5 S/m) due to oxygen removal functionalities and aromatic conjugated skeleton restoration upon graphene is to improve the electrical conductivity and also signifying superior electrochemical performance plus

higher specific capacitance of graphene is 284.3 F/g observed 1:10 (GO:NaBH$_4$) electrode at 5 mV/s. The formation of GO and reduction of graphene by borohydride were shown in **Fig. 4**.

Fig. 4. The schematic diagram for the formation of graphene oxide and schematic diagram of graphene preparation by borohydride reduction route[46].

Further, NaBH$_4$ with CaCl$_2$[47] at room temperature for 12 h. The graphene that resulted had the maximum C/O atomic ratio of 5.38 and also the least electrical resistance of graphene, which was 18.6 kΩ/sq. NaBH$_4$ in the presence and absence of sodium molybdate (Na$_2$MoO$_4$)[48] reagents and a variety of borohydrides[44,49] are used reduced for the GO.

Lithium Aluminum hydride

Lithium aluminum hydride (LiAlH$_4$) is the strongest reducing agent in synthetic organic chemistry. The reduction ability is better than that of borohydride derivative salts, which are reduced to hydroxyl groups (alcohols) to their corresponding carboxylic acids and esters. Hence, it was applied to GO to obtain graphene. Pumera and co-workers[50] prepared GO with LiAlH$_4$ and also used NaBH$_4$ and hydrazine for comparison purposes for prepared graphene.

After that, the atomic C/O ratios were obtained with reduction of LiAlH$_4$ with 12, NaBH$_4$ with 9.5, and hydrazine reductant with 11.5. From these results, the reduction clearly occurs using LiAlH$_4$ as a good reducing agent and it possessed the highest charge transfer resistance 5.9 kΩ showed the highest resistance to heterogeneous electron transfer (HET) rate based on electrochemical impedance spectroscopy. Furthermore, the ensuing graphene exhibited the least conductivity at 2.9 mS than

NaBH$_4$ at 62.4 mS, N$_2$H$_4$ 46.6 mS. The schematic reduction process of graphene was depicted in **Fig. 5**.
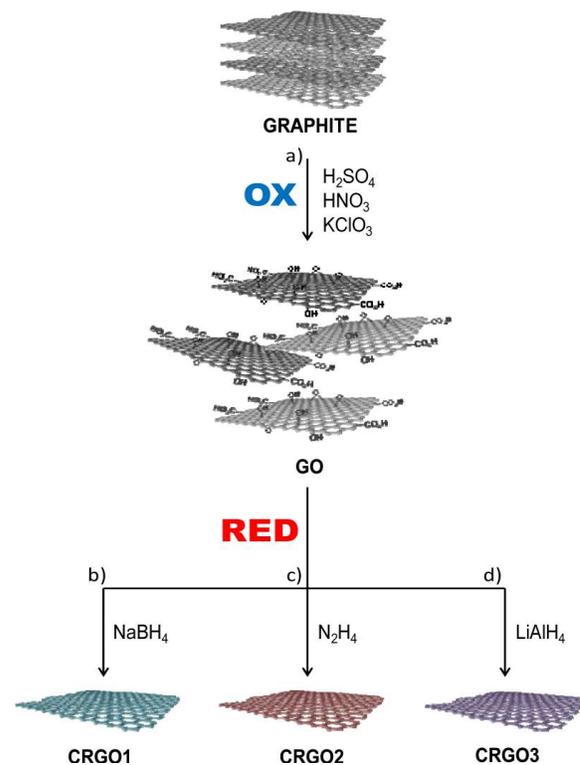

Fig. 5. The schematic representation of the procedure followed for the preparation of the graphene materials. (a) To create graphene oxide from graphite as a base material, an oxidative process was first performed. Then reduction of graphene oxide is achieved using (b) NaBH$_4$; (c) N$_2$H$_4$; (d) LiAlH$_4$.[50]

Synthesis of graphene using Oxygen containing reducing agents

Commercially, simple alcohols like methanol (MeOH), ethanol (EtOH), *iso*-propanol (*i*pr-OH), and benzyl alcohol (BnOH) showed attractive reducing ability on the way to graphene as confirmed through thermal mediated method by Bielawski and co-workers[51] were among all alcohols, more amount of reduction is observed in BnOH with the resulting graphene with retaining lamellar structure and possesses C/O ratio of 29 and 4600 Sm^{-1} electrical conductivity. In the reduction process, BnOH is direct contact with oxygen functionalities of GO, which are converted to benzaldehyde and benzoic acid in the graphene solution.

Another chemical reduction of GO through refluxing with hydroquinone in an aqueous ethanolic mixture was studied by Yao and co-workers[52]. Hydroquinone functions like a reducing agent, losing one H^+ to generate a mono phenolate ion or 2 H^+ to generate a di phenolate ion in the form of quinone. The resultant graphene shows hydrophobic and dispersion stabilities in water for a few hours. Further, the production of graphene was reported with ethanol vapour at 900 ^oC[53], and gallic acid in presence of ammonia[54].

Synthesis of graphene using Sulphur containing reducing agent

Bangal and co-workers[55] were used to compounds of sulphur like $NaHSO_3$, $Na_2S_2O_3$, Na_2SO_3, $SOCl_2$, $Na_2S.9H_2O$, SO_2 are used as a reagent for the reduction of GO. The reaction was maintained in a mixture of GO in $DMAc/H_2O$. Among all these reagents, $SOCl_2$ is a superior reagent, even the exothermic nature upon contact with the aqueous phase, then form HSO_3^- anion readily contacts with GO with resulting graphene shows a C/O ratio of 8.48 and remaining reducing agents are also followed with similar HSO_3^- anion route for reduced graphene. Inspired by the above results, Few and co-workers[56] were applied for the usage of sodium hyposulphite ($Na_2S_2O_4$) for reduction of GO in alkaline solution (NaOH) for 15 min and the resulting graphene with conductance is 1377 Sm^{-1}. The NaOH was present in the suspension to act as both stabilizer and catalyst. Here $S_2O_4^{-2}$ nucleophile attack on the oxygen functionalities (alcohols, epoxides) of GO oxidizes to SO_3^{-2} followed by the release of water molecule led to the formation of graphene.

Sulphur contains as one of the thiourea dioxide precursors which is used to demonstrate the deoxygenation of carbonyls, aromatic nitro, hydrazo, azo, azoxy, and organosulphur compounds. To use thiourea dioxide[57] in a basic medium with the process of single electron transfer resulting in urea and sodium sulphite formation as byproducts. On these observations, with the help of thiourea dioxide was used to the manufacturing of graphene for large-scale productions. Pumera and co-workers[58] reported the reduction of GO used to thiourea dioxide in alkaline

medium (NaOH) carried out for up to 20 h (9 h, 2 h, 5 h, 20 h) were shown in **Fig. 6**.

Fig. 6. The functional groups of GO reduced by thiourea dioxide[58].

The graphene structure and electrochemical characteristics were obtained after a one-hour process. The resulting graphene had a C/O ratio, 14.5, and a charge transfer resistance as low as 0.11 $k\Omega$, which was lower than GO's 5.43 $k\Omega$.

Fugestu and co-workers[59] suggested a comparable reduction ability of thiourea in an alkaline (NaOH) medium. Sodium chlorate was used as a stabilizer to maintain the high stability in an aqueous solution of graphene and showed a 5.89 C/O ratio and conductivity 3205 Sm^{-1}. These results said that thiourea dioxide is a superior reductant to sodium hydrosulfite[56]. The production of graphene from GO by thiourea in a basic medium were depicted in **Fig. 7**.
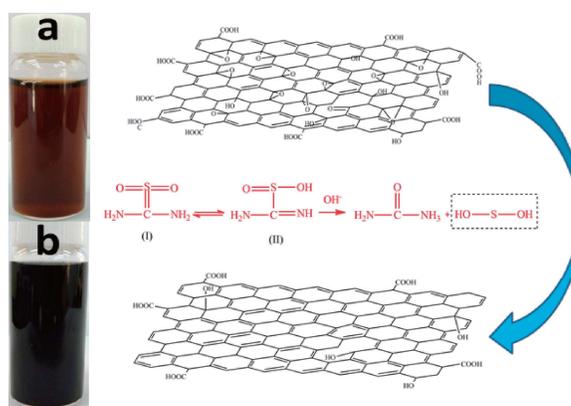

Fig. 7. The production of graphene (b-block solution) from GO (a-aqueous brownish yellow solution) using thiourea in presence of NaOH[59].

Consequently, Wang and co-workers effort to produce bulk graphene preparation with thiourea[60] at 8 h duration of reaction of obtained graphene with 5.6 C/O ratio and 635 Sm^{-1} electrical conductivity and

excellent dispersion in organic solvents (Ethanol and DMF).

Fujita and co-workers[61] reported for graphene using ethanethiol-aluminium chloride, which exposed efficient defunctionalization of alkoxyl, peroxy, hydroxyl, alkylthio and halo groups from parent aromatic groups based on a one electron transfer process. The resultant graphene exhibited a C/O ratio of 4.71. Further, the graphene showed dispersion stability in aqueous media and electrochemical impedance spectroscopy displayed a minimal charge transfer resistance of 0.09 kΩ (graphite oxide: 4.56 kΩ, bare glassy carbon: 0.55 kΩ). Further, Lawesson's reagent[62,63], and Thiophene[64], etc. are used for the production of graphene.

Synthesis of reduced graphene by metal acid as reducing agents

By the usage of metal with acid medium for the reduction process has considerably produced graphene skeleton. The fast and effective reduction capabilities of this reaction mixture were used to reduce GO, but few reasons are not clear to access for the reducing capability for graphene experiments. Despite these reasons, the reduction involves using metal in the acid medium was achieved electron translocation among metal & Graphene oxide (GO).

Firstly, Fan with co-workers[65] has accomplished the GO reduction using Aluminum (Al) with hydrochloric acid (HCl) mixture at room temperature in 30 min. typically, 1 g of Al powder and 10 mL HCl (35 wt%) into 200 mL GO suspension (1 mg/1mL), the reaction was carried in 30 min at room temperature. After that, to remove the excess Al powder by addition of 5 mL of HCl (0.5 M) was mixed into the above suspension. Later the RGO washed filtered, washed with water and ethanol, and dried at 90 $^{\circ}$C for 3 h. The resultant graphene possesses C/O ratio of 18.6 and electrical conductivity of 2100 Sm^{-1}.

The standard reduction potential of aluminum (-1.68 V) was significantly more negative than sodium borohydride (-1.24V) and hydrazine hydrate (-1.16V). Alone Al is not possible to reduction for GO in the absence of HCl, wherein the presence of HCl dissolving an Al_2O_3 on Al's surface thus improvising reduction capability. Al reacts with

H^+ to produce Al^{+3} (Al_2O_3) and then GO results with a negatively charged surface adsorbed with Al^{+3} particles. By the contact of Al with GO in reduction gives a large amount of heat that could be produced with the liberation of bubbled pure hydrogen gas and aggregates with thick sheets in wide range distribution sizes of graphene sheets. The electrostatic attraction between RGO and Al possess by the electron transfer process.

According to the above group, the graphene obtained from the reaction GO with iron powder in presence of HCl in 6 h[66]. The resulting graphene displayed C/O ratio of 7.9 and measured 2300 Sm^{-1} electrical conductivity. It shows a lower I_D/I_G ratio of 0.32 than GO (0.86), suggesting the restoration of the sp^2 carbon network on graphene. The graphene (GNS) based on Fe reduction was illustrated in **Fig. 8.**
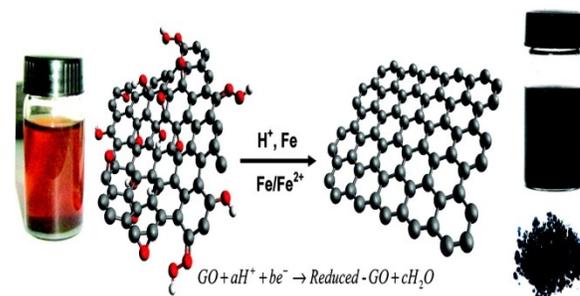

Fig. 8: The illustration of the preparation of graphene (GNS) based on Fe reduction[66].

Continuously, the graphene was produced by utilizing metal in an acidic medium such as zinc powder in HCl[67], Zinc fillings and sulphuric acid (H_2SO_4)[68], Aluminum foil and HCl[69], Tin (II) chloride in HCl[70], and Magnesium in HCl[71], etc.

Synthesis of reduced graphene by metal in basic medium as reducing agents

The reduction of GO in the presence of metal in the basic medium like ammonia (NH_3), sodium hydroxide (NaOH), etc. Wang and co-workers[72] have studied the capacity of zinc powder within the solution of ammonia to graphene in 10 min with a C/O ratio, 8.09 and exhibited a capacitance of 116 Fg^{-1}. The reduction possibility was proceeding through a Zn-graphene oxide primary battery system. Where anode is zinc (Zn) and cathode is GO in

ammonia as an electrolyte. Hereby, the Zn had been oxidized to give free electrons which lead to NH_4^+ conversion to NH_3 and nascent H and to form the zinc ammonia complex. While the hydrogen (H) reacted with removing of hydroxyl and epoxide groups on GO to form graphene. In addition to further examined by using zinc powder in NaOH solution[69], Na-ammonia system[73], etc. were used.

Conclusion

This review outlined the formation of graphene by reduction of GO as the most fascinating topic. Among the many methods developed by various research workers for the production of graphene-based on different reduction strategies on GO, a mainly wet-based chemical reduction is considered to be the finest convectional method. Although, the chemical approaches are promising for the industrial production of graphene for numerous applications, utilizing these chemical reductants has toxic properties, which may concern the environment as well as living organisms, in biomedical applications and pollution problems, etc. Further, the Large-scale production of individual graphene sheets is still challenging although several methodologies have been developed for commercial and industrial applications.

Conflict of interest
All the authors declare no conflict of interest to the present review article.

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