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A comparative study of organic solvents, ionic liquids, surfactants and acids for liquid phase exfoliation of graphene

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Graphene is the most widely investigated carbon nanomaterial having two-dimensional honeycomb lattice structure. Recently, it has attracted worldwide attention due to its remarkable electrical, thermal, mechanical, chemical and optical properties, which are highly suitable for various electronic device applications. Various methods of graphene synthesis have been utilized for the production of graphene each having its own advantages and disadvantages. Liquid phase exfoliation method uses top-down approach and has the advantages of being environment friendly, facile and economically viable. Liquid phase exfoliated graphene is highly suitable for making thin films for their potential applications in electronic devices such as thin films transistors, transparent electrodes, light-emitting diodes, supercapacitors, etc. In this paper, a comparative study of different exfoliation medium used for liquid phase exfoliation of graphene such as organic solvents, ionic liquids, surfactants, polymers and acids are described. Because of the usually low concentration of graphene (< 0.01 mg/mL) obtained from liquid phase exfoliation method, research has been done for enhancing the concentration. Recent progress made in enhancing graphene concentration in organic solvents by adding various additives is reported here. Finally, we discuss the challenges and future prospects of improving liquid phase exfoliation of graphene for modern electronics devices.

Keywords: Graphene synthesis, Liquid phase exfoliation, Organic solvents, Surfactants, Concentration enhancement

1 Introduction

Graphene is a two-dimensional structure of sp^2-hybridised hexagonally bonded carbon atoms as shown in Fig. 1(a). Its natural precursor, graphite consists of a number of graphene sheets bonded together by the Van der Waals forces between graphene layers as shown in Fig. 1(b). Graphene is the basic building block of other allotropes of carbon atoms like carbon nanotubes, fullerenes[1], etc. Graphene has become one of the most investigated materials because of its excellent electrical, optical, thermal, structural and chemical properties. Some of the exotic properties of graphene are shown in Fig. 2. Graphene exhibits an unusual quantum Hall effect[2], tunable band gap[3], charge carriers mobility of 10000 $cm^2\ V^{-1}\ s^{-1}$ at room temperature[4,5], high thermal conductivity of 5000 $W\ m^{-1}\ K^{-1}$ which is 10 times higher than copper[6] and optical transparency[7] of 97.7%. Graphene exhibits high specific surface area[8] of 2630 $m^2\ g^{-1}$ and Young's modulus of 1 TPa[9]. Graphene can be modified chemically to get other desired properties for various applications[10]. Some of the potential applications of graphene are transistors[11], liquid crystal devices[12], biological sensors[13,14], energy storage devices[15], electrochemical capacitors and solar cells[16]. Recently, various methods have been utilized for the synthesis of graphene which follows either bottom-up or the top-down approach. The bottom-up approach uses chemical reactions in which individual carbon atoms join together to form hexagonal graphene structure. Top-down approach uses processes such as sonication for converting graphite

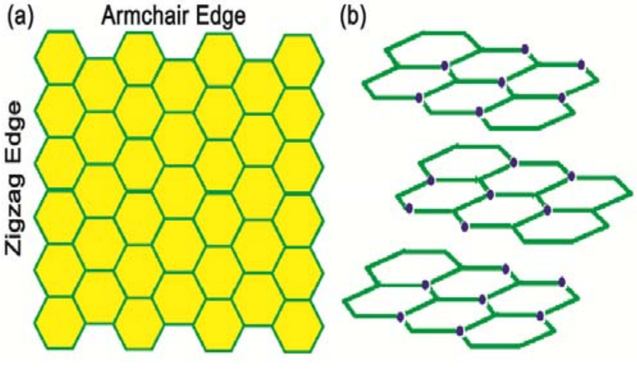

Fig. 1 — Schematic diagram showing (a) two-dimensional hexagonal honeycomb structure of graphene and (b) structure of graphite made up of many graphene layers.

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*Corresponding author (E-mail: mr_randhir_singh@yahoo.co.in) powder into graphene nanosheets. The prominent graphene synthesis routes are mechanical exfoliation[17], chemical vapour deposition (CVD) [18], epitaxial growth on silicon carbide[19] and the reduction of graphene oxide[20]. The main disadvantage of most of the graphene methods is that the graphene produced by these methods has low quality and high defects. Low quality graphene with defects is not suitable for various electronic device applications.

The chemical vapor deposition (CVD) synthesis method is normally used for the mass production of graphene for electronics device applications. But because of the complicated process parameters such as temperature, gas flow kinetics and fluid dynamics along with precise control of precursor for controlled growth of graphene on different substrates, this method is not feasible at the laboratory level. CVD is an example of bottom-up approach and has the disadvantage of being limited to specific environmental parameters like pressure, temperature, etc. Another graphene synthesis method known as hummer's method converts graphite into graphite oxide and finally into graphene oxide. The graphene oxide is further reduced into reduced graphene oxide (RGO). Besides being a lengthy process, such produced RGO possesses various structural defects which greatly degrades its electronic properties[21] and makes it unsuitable for electronic device applications. Prominent graphene synthesis methods with their advantages and disadvantages are listed in Table 1.

Because of the limitations of earlier graphene synthesis methods a new method known as liquid phase exfoliation method was reported by Coleman *et al.*[22] in 2008. This method was based on the assumption that nanosheets or nanotubes can be dispersed in some solvents using sonication. As prepared, graphene nanosheets can be filtered to form graphene films on filter paper for further study and characterization as shown in Fig. 3. The graphene synthesized by liquid phase exfoliation method exhibits good electrical and structural properties and is free from oxides and defects[23,24]. Hence, liquid phase exfoliation is a simple and economical method of making high-quality graphene and can be investigated further to increase the graphene yield and enhancement of exfoliation efficiency.

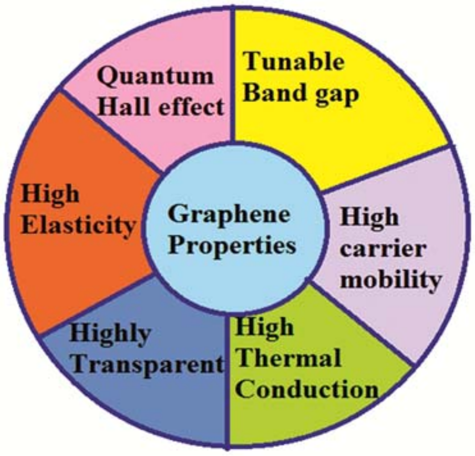

Fig. 2 — Schematic diagram showing different exotic properties of graphene.

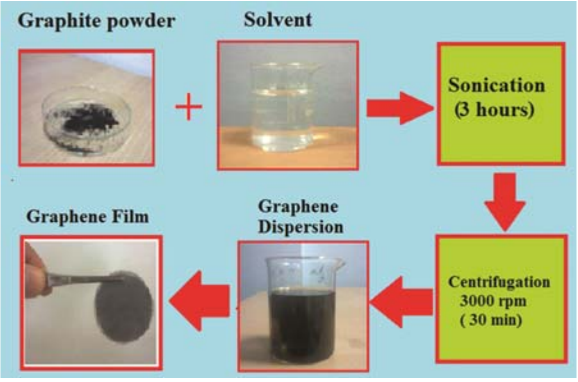

Fig. 3 — Various steps involved in the liquid phase exfoliation process using sonication.

Table 1 — Prominent graphene synthesis methods with their advantages and disadvantages.

Graphene synthesis method	Advantages	Disadvantages
Mechanical exfoliation method	Good quality, Low yield	Not a scalable process, Low yield
Chemical vapour deposition	High quality, large area graphene	High temperature and low vacuum conditions
Epitaxial growth on SiC	Large continuous film, good quality	High temperature and low vacuum conditions Not transferable
Hummer's method	High Yield	High defects in graphene, Harmful chemicals used
Electrochemical exfoliation	Lesser time, facile	DC voltage and electrolytes requirements
Liquid phase exfoliation	Easy, Safe, high quality	Long sonication time requirement , low graphene concentration

Here, the recent progress made in the liquid-phase exfoliation of graphene in various exfoliating medium is reported. We discuss the quality and yield of the liquid phase exfoliated graphene in various solvents through the characterization details. Various additives and salts used to enhance the graphene concentration in organic solvents are also discussed. Finally, the prospects and challenges for improvement of liquid phase exfoliation of graphene are discussed.

2 Graphene from Graphite

The graphite has a crystalline structure[25] having a number of graphene sheets stacked together over each other by van der waals forces. The interlayer distance between two adjacent graphene layers in graphite[26] is 0.34 nm. This Van der Walls force between adjacent graphene layers in graphite is weak[27] and can be overcome for exfoliating the individual graphene sheets. By increasing the interlayer distance between adjacent graphene sheets using graphite intercalation technique, the attractive forces between them can be overcome. The solvent molecules intercalate on graphene layers and results in graphene exfoliation as described in Fig. 4. This process overcomes the van der walls force because it is proportional to $1/r^6$ where r is the distance between the molecules[28]. It has been found that for an interlayer distance of more than 5 Å van der walls force completely vanishes and individual graphene sheets separates from bulk graphite[29,30].

The main criterion for choosing the solvent for graphene liquid phase exfoliation is its surface tension. It has been reported that solvents having surface tension in the region of 40–50 mJ/m^2 are the most suitable for liquid phase exfoliation of graphene. Solvents like N-methyl-2-pyrrolidone (NMP), *N,N*-dimethylacetamide (DMA) and *N,N*-dimethylformamide (DMF) have surface energies which matches with graphene. Other solvents like ethanol, acetone which have surface energies lesser than graphene make them unsuitable for graphene exfoliation[31]. Graphene has been reported to be exfoliated in both aromatic and non-aromatic solvents[32]. It has been found that, during graphene intercalation process, transfer of charge between the solvent molecules and graphene layers result in separation of individual graphene layers[33–35]. This exchange of charge has also been observed in nanotubes[36] and fullerenes[37]. Hence, the exfoliated graphene sheets are either negatively or positively charged[38], depending upon the solvent used. The repulsion between the similarly charged graphene layers prevents their aggregation[39] and helps in the stability of graphene nanosheets. This phenomenon of charge transfer occurs in ionic liquids[40,41] and chlorosulphonic acid[42] also. Some surfactants and polymers have been reported to be useful for the exfoliation of graphene sheets in water[43,44].

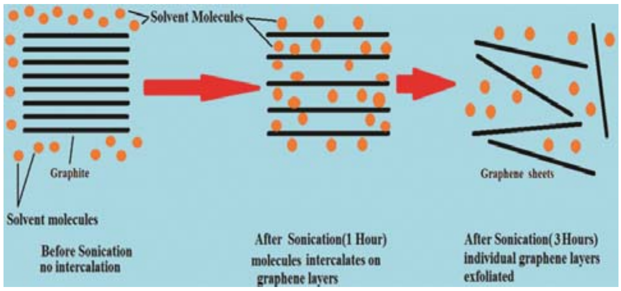

Fig. 4 — Graphene synthesis mechanism involved in the liquid phase exfoliation process.

3 Graphene Exfoliation in Organic Solvents

Because of hydrophobic nature of graphite, organic solvents are the better exfoliation medium than water. Solvents that have been found useful in making carbon nanotubes (CNTs) dispersions are considered suitable for graphene exfoliation. It has been found that a particular solvent is suitable for graphene exfoliation if its surface tension lies in 40–50 mJ/m^2 range and if its Hansen solubility parameters meet a specific criterion[45].

NMP is widely used for graphene exfoliation because its surface tension and Hansen solubility parameters both have the appropriate values as required[46]. Sonication of graphite powder in NMP organic solvent for 30 min and later centrifugation at 500 rpm for 90 min can produce graphene dispersions of 0.01 mg ml^{-1} concentration. TEM results of as prepared graphene sheets show single, bi-layered and folded graphene nanosheets as shown in Fig. 6 (a and b).

SEM results of as prepared graphene sheets in NMP solvent are shown in Fig. 5(a and b). From the SEM images we observe that graphene nanosheets have lateral sizes as small as 785 nm and 986 nm. Raman spectrum of the graphene produced using NMP solvent shows D-peak, G-peak and 2D peak, which confirms the formation of graphene nanosheets as shown in Fig. 7(a). The intensity of D-peak is directly proportional to the defects present in graphene[47]. The smaller value of *D*/*G* peak ratio (1.01) as compared to those observed in GO and reduced GO samples[48] confirms the lesser amount of defects present in liquid phase exfoliated graphene.

Figure 7(b) shows that thin graphene film prepared by vacuum filtration method on PTFE membrane filter exhibits high conductivity after annealing. XRD diffraction patterns of graphene produced by NMP solvent shown in Fig. 8(b) has peak intensity at lower angle than the value of pure graphite shown in Fig. 8(a).This confirms that liquid phase exfoliated graphene has increased interplanar spacing than graphite.

Usually a very low concentration of graphene is obtained by liquid phase exfoliation which is less than 0.01 mg/mL. In order to enhance the graphene concentration the sonication time is increased. By increasing the sonication time the process becomes too lengthy, time-consuming and impractical. A concentration of 1.2 mg mL^{-1} has been reported with the sonication in NMP solvent for a long period[49] of 460 h. Another disadvantage of increasing the sonication time is that the size of the graphene nanosheets decreases due to sonication-induced scissions.

4 Graphene Exfoliation in Acids

Some acids have been found useful in liquid phase exfoliation of graphene. Methanesulfonic acid can produce a graphene concentration of 0.2 mg mL^{-1} by sonicating graphite for about 2 hours using water bath sonicator[50]. Another acid that has been found useful in graphene exfoliation is chlorosulfonic acid. Chlorosulfonic acid is a very strong acid which does not require even sonication for graphene exfoliation. Graphene concentrations up to 2 mg mL^{-1} can be achieved by using this acid without sonication.

The reason for this rapid exfoliation without sonication is the repulsion between graphene layers due to protonation of the graphitic layers. Carbon nanotubes have also exhibited similar protonation phenomenon[51]. It has been reported by Lu *et al.*[52] that chlorosulfonic acid can be mixed with H_2O_2 to reduce the exfoliation time of graphene to nearly few seconds and to increase the yield up to 95%. It is due to the release of large amount of heat due to formation of Caro's acid as a result of mixing of chlorosulfonic acid and H_2O_2[53]. The graphene produced by this method shows the absence of the D peak in the Raman spectrum indicates the high quality of graphene inspite of the oxidizing nature of chlorosulfonic acid and hydrogen peroxide.

Ortho-dichlorobenzene (ODCB) is another organic solvent suitable for graphene exfoliation because its surface tension 36.6 mJ m^{-2} is close to the required range of surface tension[54]. With the sonication of graphite in ODCB for 4 h graphene dispersions with concentration of 0.03 mg mL^{-1} can be obtained after centrifugation at 4500 rpm for 30 min.

As the sonication time increases more than five hours the quality of graphene decreases in ODCB

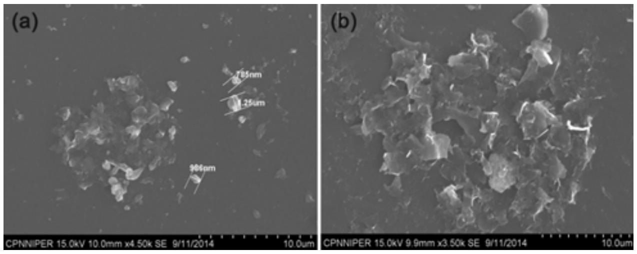

Fig. 5 — SEM images of multilayered graphene nanosheets exfoliated in NMP solvent.

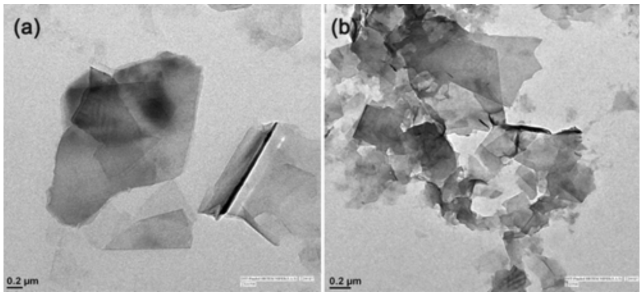

Fig. 6 — TEM results of (a) multilayered graphene nanosheets exfoliated in NMP solvent and (b) overlapped single and few-layered graphene nanosheets exfoliated in NMP solvent.

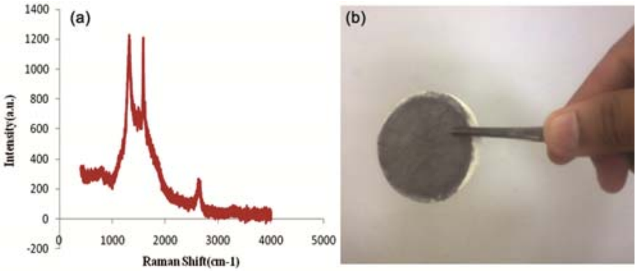

Fig. 7 — (a) Raman spectrum of graphene liquid phase exfoliated in NMP solvent and (b) graphene film prepared by vacuum filtration technique.

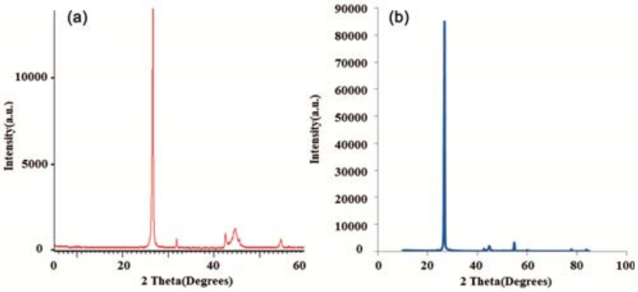

Fig. 8 — (a) XRD diffraction pattern of pure graphite powder used for graphene synthesis and (b) XRD diffraction pattern of graphene liquid phase exfoliated in NMP organic solvent.

organic solvent. The morphology of the as prepared graphene nanosheets is studied from the TEM and SEM images. The TEM and SEM images of the prepared graphene nanosheets shows that graphene nanosheets have lateral width from 500 nm to few µm as shown in Fig. 9(a) and (b) and Fig. 10(a) and (b), respectively. Thin graphene films can be fabricated from the as-prepared graphene dispersion by vacuum filtration method on polytetra fluoroethylene (PTFE) membrane filter and thermal annealing can be used to increase the conductivity of the graphene film.

5 Graphene Exfoliation using Surfactants

Organic solvents have been found suitable for graphene exfoliation, but these solvents are toxic in nature and are expensive. Because the organic solvents are difficult to remove and are not biocompatible, hence, they are not the best choice for graphene exfoliation. Due to these limitations of the organic solvents, water is regarded as the better exfoliating medium for graphene. Because of the hydrophobic nature of graphene it cannot be exfoliated directly in water but various surfactants can be utilized for graphene exfoliation. By adding surfactants in water its surface tension can be decreased so as to match it with that of graphene, hence making exfoliation possible. Surfactants facilitate sonication process to stabilize the exfoliated graphene sheets so as to prevent them from re-aggregation. Thus, surfactants help in making homogeneous and defect-free graphene dispersions[55].

Surfactants used for graphene exfoliation are of two types: ionic and non-ionic surfactants. Sodium dodecylbenzenesulfonate (SDBS) is the widely used ionic surfactant, for the liquid-phase exfoliation of graphene in water. It has been reported that by sonicating a mixture of water, graphite and SDBS for 30 min and centrifugation at 500 rpm for 90 min, graphene concentration upto 0.05 mg mL^{-1} can be obtained. Graphene produced by this method have single and few-layered graphene nanosheets. Another surfactant that has been found useful for graphene exfoliation is sodium cholate. By using this surfactant graphene dispersions with concentration up to 0.3 mg mL^{-1} can be obtained in water/sodium cholate solution after sonication for 430 h. Graphene films prepared by this exfoliated graphene exhibited high conductivity of 7000 S m^{-1} without annealing and 17500 S m^{-1} with annealing at 500 °C. Sonication process can be performed either with water bath sonicator or by using tip horn sonicator. Graphene exfoliation in water/sodium cholate solution using horn sonication has been reported by Green and Hersam[56].

This produced a graphene concentration of 0.09 mg mL $^{-1}$ in water after tip sonication and centrifugation at 15,000 rpm for 60 min.

Both ionic and non-ionic surfactants have different effects on the exfoliation of graphene. The effect of different ionic and nonionic surfactants on the graphene exfoliation has been reported by Smith *et al.*[57] They found that solubility of graphene in water is directly proportional to electrostatic potential and steric potential barriers for ionic and nonionic surfactants. Table 2 shows various ionic and non-ionic surfactants used for the liquid phase exfoliation of graphene.

Guardia *et al.*[58] investigated the graphene exfoliation using both ionic and nonionic surfactants. Graphene concentration of upto 1 mg mL^{-1} can be obtained by mixing graphite and pluronic P-123 after sonicating for 2 hours. As prepared, graphene films produced by vacuum filtration exhibited high electrical conductivity of 1160 S m^{-1}. Graphene prepared by using nonionic surfactant have great scope for use in biomedical applications.

6 Graphene Exfoliation in Ionic Liquids

Ionic liquids are the new class of liquids that are being investigated for the graphene exfoliation. Ionic

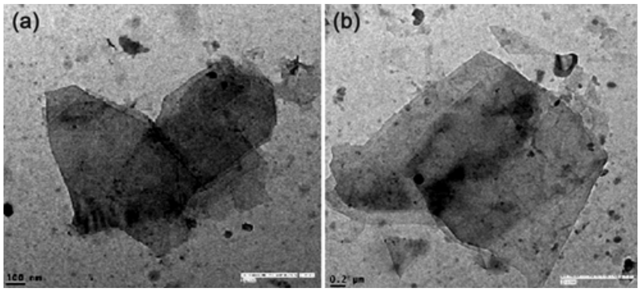

Fig. 9 — (a) TEM results of multilayered graphene nanosheets exfoliated in ODCB solvent and (b) overlapped single and few-layered graphene nanosheets exfoliated in ODCB solvent.

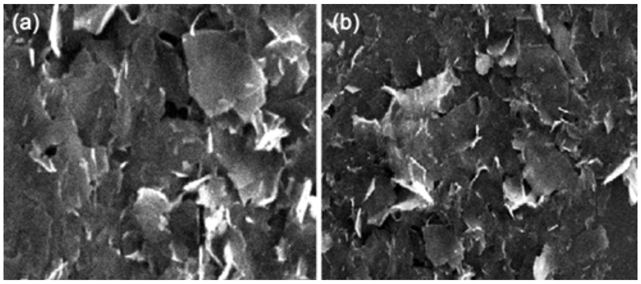

Fig. 10 — SEM results of multilayered, overlapped graphene nanosheets exfoliated in ODCB solvent.

Table 2 — Ionic and non-ionic surfactants used for graphene liquid phase exfoliation.

S. No.	Surfactant name	Acronym	Surfactant type
1	Sodium Deoxycholate	DOC	Anionic
2	Hexadecyltrimethylammonium bromide	CTAB	Cationic
3	Brij 35	B35	Non-ionic
4	Dodecyltrimethylammonium bromide	DTAB	Cationic
5	L-Tryptophan	LTP	Amino acid
6	Poly(Carboxylate)	PC	Anionic
7	Poly(ethyl cellulose)	PEC	Non-ionic
8	Pluronic F-108	PF-108	Non-ionic
9	Pluronic F-127	PF-127	Non-ionic
10	Sodium dodecyl sulfate	SDS	anionic
11	Sodium dodecylbenzene sulfonate	SDBS	anionic
12	Sodium binol salt	SBS	anionic
13	Sodium Cholate	SC	anionic
14	Tween60	T 60	Non-ionic
15	1,3,6,8 pyrenetetrasulfonic acid	TPA	anionic
16	Sodium taurodeoxycholate	TDOC	anionic
17	7,7,8,8-tetracyanoquinodimethane	TCNQ	anionic
18	Tetradecyltrimethylammonium bromide	TTAB	Cationic

liquids are the special salts which remain in the liquid state at temperatures lower than 100 °C[59, 60]. Some of the important properties of ionic liquids are that they are highly nonvolatile and are thermally and chemically stable[61]. Ionic liquids have surface tension close to that of graphene[62] and are highly compatible with many organic and inorganic solvents[63]. Some ionic liquids have been utilized as solvents for dispersing carbon nanotubes[64]. Ionic liquids have also been used for the electrochemical exfoliation of graphene[65]. The electrostatic interactions between ionic species and the *p* electrons of graphene sheets is considered as the main reason for the efficient exfoliation and stabilization of graphene sheets[66,67].

Ionic liquid 1-butyl-3-methyl-imidazolium bis (trifluoromethanesulfonyl)-imide has been utilized by Wang *et al.* as the graphene exfoliation medium. Graphene concentration of up to 0.95 mg mL^{-1} was obtained after tip sonication for 60 min and centrifugation at 10000 rpm in this ionic liquid. The majority of graphene nanosheets obtained by using this ionic liquid were having lateral lengths of few µm and their thickness was found to be few layers. Another ionic liquid 1-hexyl-3-methyl-imidazolium hexafluorophosphate, has also been used for preparing graphene using sonication. By using this ionic liquid graphene dispersions were obtained with a concentration of 5.33 mg/mL after 24 h of sonication. The lateral size of the graphene sheets obtained by using this ionic liquid was 4 µm having thickness of graphene sheets as 2 nm. Ionic liquids have lower volatility, which eliminates requirement for environmental release because of contamination. The disadvantage of ionic liquids is their aquatic toxicity. Many of the ionic liquids are combustible in nature, so careful handling is required.

7 Graphene Exfoliation using Polymers

Graphene has been reported to be exfoliated in water[68–70] and organic solvents[71,72] with the help of various polymers like polyvinylchloride, polyvinyl acetate, polycarbonate, polymethyl methacrylate etc. Coleman *et al.* reported that maximum graphene concentration is obtained if Hildebrand solubility parameters of solvent and polymer match with that of graphene sheets. Because of low graphene concentration of 0.022 mg mL^{-1} obtained in tetrahydrofuran(THF) and 0.141 mg mL^{-1} in cyclohexanone, there is a need of a suitable polymer–solvent mixture for obtaining high graphene concentrations. It has been reported that a higher graphene concentration of 0.045 mg mL^{-1} in THF and 0.18 mg mL^{-1} in chloroform was obtained if hyper branched polyethylene (HBPE) was used as the stabilizing agent. HBPE is made by ethylene chain walking polymerization method[73]. HBPE has been reported to solubilize carbon nanotubes[74]. Polyvinylpyrrolidone (PVP) is the polymer that acts as a stabilizing agent for graphene dispersion. Polyvinylpyrrolidone (PVP) - stabilised graphene dispersion has been reported by Bourlinos *et al.*[75] Graphene concentration upto a concentration of 0.1 mg mL^{-1} has been achieved by sonication for 9 hours and centrifugation at 1500 rpm for 30 min. The main advantage of this method is that because PVP is biologically safe and inexpensive polymer. The graphene produced by this can be highly useful for biomedical applications. Using polymers in the liquid phase exfoliation of graphene greatly enhances the exfoliation efficiency. With polymers graphene is exfoliated in liquids, which is otherwise not possible. Graphene can be successfully exfoliated in water by using PVP polymer. The main disadvantage is that due to strong polymer–graphene interactions, most of the graphene is required to be extracted from graphene–polymer composites. For solving this, one approach is to wash it with a solvent which can dissolve PVP polymer from graphene sheets. It has been reported that by washing with ethanol – chloroform mixture and centrifugating at 4000 rpm for 10 min, the graphene yield can be increased.

8 Graphene Exfoliation using Pyrenes

Water is the best non-toxic liquid for graphene exfoliation, which can be useful for biomedical applications[76]. Graphene exfoliation in water is a difficult task because of its hydrophobic nature. This problem is solved by using various surfactants[77–92]. The polycyclic aromatic hydrocarbons have been found useful in graphene exfoliation because of their p–p stacking interactions with graphene sheets[93-99]. Pyrenes have been reported to be used for the stabilization of carbon nanotubes and graphene dispersions[100]. Because of pyrene adsorption onto graphene sheets through p–p interactions the surface free energy of the dispersion decreases, which helps in the exfoliation of graphene sheets. Figure 11 shows structures of various pyrene derivatives used in liquid phase exfoliation of graphene.

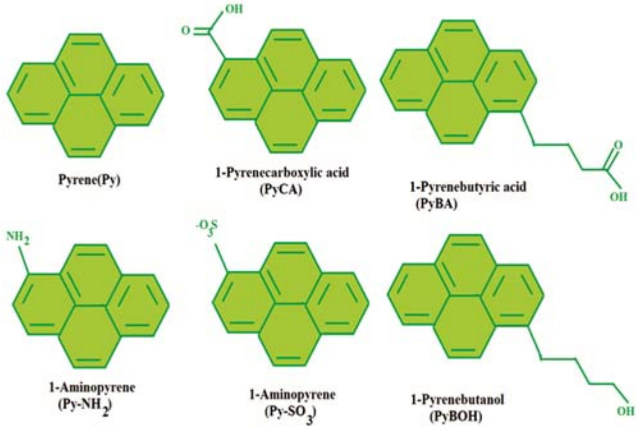

Fig. 11 — Structures of various pyrene derivatives used in liquid phase exfoliation of graphene.

It has been reported by He and co-workers that single layers of graphene sheets can be exfoliated by using 1,3,6,8-pyrenetetrasulfonic acid tetrasodium salt (Py–$(SO_3)_4$).

Another pyrene derivative aminomethylpyrene (Py–Me–NH_2) has been used to exfoliate graphene for fabrication of transparent conductive films[101]. It has been reported by Shi *et al.*[102] that by using pyrenebutyrate and pyrenesulfonic acid sodium salt (Py–SAH) graphene sheets can be stabilized in water, which can be used for fabrication of electrochemical and solar cells. Green and co-workers investigated pyrene, 1-aminopyrene, 1-aminomethyl pyrene, 1-pyrenecarboxylic acid, 1-pyrenebutyric acid, 1-pyrenebutanol, 1-pyrenesulfonic acid hydrate, 1-pyrenesulfonic acid sodium salt for the exfoliation of graphene. Among these pyrene derivatives the Py–SO_3 was most effective in enhancing graphene exfoliation efficiency with a maximum concentration of 1 mg/ml. The graphene sheets stabilized by Py–SO_3 were found to be 2–4 layers thick.

9 Graphene Concentration Enhancement

Usually the yield of liquid phase exfoliation method is very low (<0.01 mg/mL). There is a need of scalable mechanism for increasing the graphene yield. For solving this purpose, the sonication time can be increased, concentration enhancing agents can be added to the organic solvents and thermal treatment can be provided to increase the graphene yield. Concentration enhancing salts can be added to organic solvents to increase the yield. It has been reported by Liu and Wang[103] that by adding sodium hydroxide (NaOH) the exfoliation efficiency can be increased in NMP, DMA and cyclohexanone due to intercalation process. It has been observed that by adding NaOH to NMP, the graphene yield can be increased to 3 times its original concentration. XRD spectrum of graphene after adding NaOH shows a decrease in the diffraction angle at peak intensity, which indicates the expanded interlayer distance due to intercalation of NaOH onto the individual graphene layers. Another compound which increase the graphene exfoliation yield in NMP has been reported by Geng *et al.*[104] is tetrabutylammonium hydroxide (TBA). If porphyrin is added with TBA it acts as the stabilizing agent which makes graphene more soluble in NMP. TBA and porphyrin if added simultaneously in NMP helps in the intercalation of organic ammonium ions as noticed in the case of graphite oxide[105], increases graphene solubility in NMP. It has been reported by Oh *et al.*[106, 107] that by giving thermal treatments the interlayer spacing of graphite increases which helps in the graphene exfoliation in NMP solvent.

It has been found that salts can be used to improve the graphene exfoliation efficiency in organic solvents like NMP. Organic salts like potassium sodium tartrate(PST), sodium tartrate(ST), sodium citrate(SC) and edetate disodium(ED) have been reported to be useful for the exfoliation of graphene in organic solvents NMP, DMF and DMSO[108]. Figure 12 shows the enhancement in graphene concentration as a result of addition of organic salts sodium tartrate(ST), sodium citrate(SC) and edetate disodium(ED) in DMSO organic solvent.

From Fig. 12 we see that sodium citrate (SC) salts are most suitable for enhancing graphene concentration in DMSO solvent. By adding these organic salts the exfoliation efficiency was enhanced considerably with simple sonication of few hours. The resulting graphene concentration was close to 1 mg mL^{-1} and the obtained graphene was defect free.

This is a simple, facile and economical method of preparing high-quality, defect-free graphene.

By adding additives like anthracene the graphene concentration is found to be enhanced in solvents NMP, ODCB, DMSO and benzonitrile (BZN) as shown in Fig. 13. From Fig. 13 we observe that by adding anthracene a maximum concentration of 0.04 mg/mL is obtained in NMP solvent.

It has been found that by adding various organic salts graphene concentration was found to enhance in

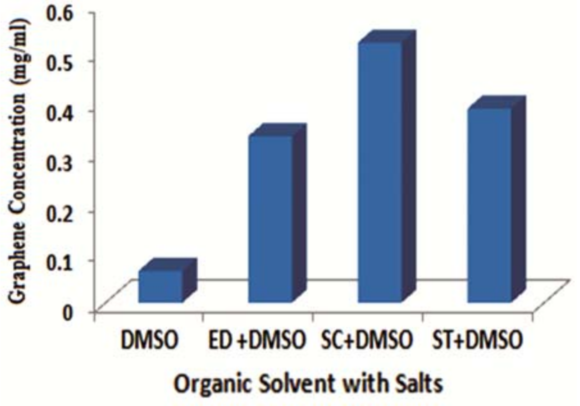

Fig. 12 — Enhancement in graphene concentration with addition of organic/inorganic salts in DMSO organic solvent.

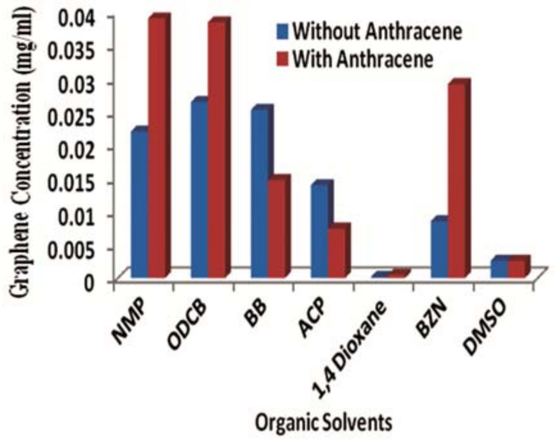

Fig. 13 — Enhancement in graphene concentration with addition of anthracene in NMP, DMSO, ODCB, BZN, BB, ACP and 1,4-dioxane organic solvents.

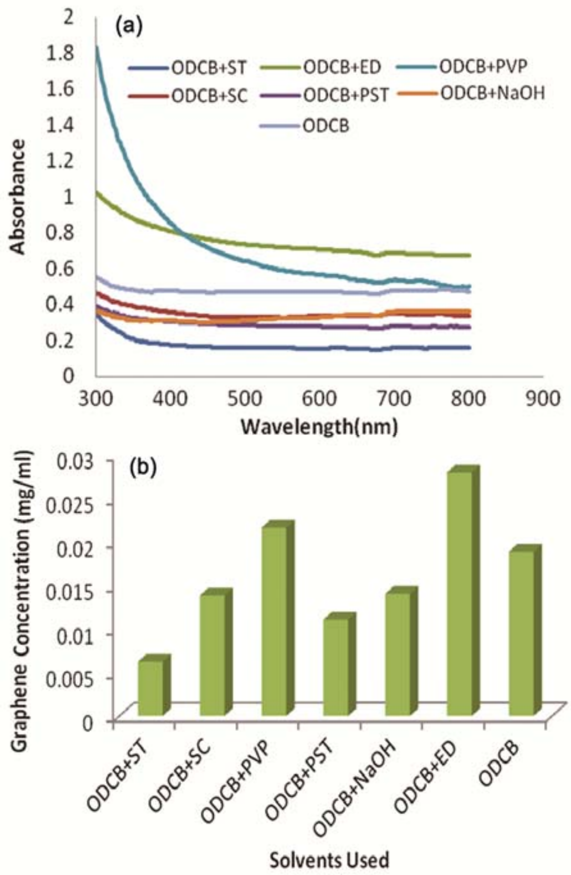

Fig. 14 — (a) UV-vis spectra of graphene dispersion obtained in ODCB after adding different organic salts and (b) comparison of graphene concentration obtained in ODCB organic solvent after adding different organic salts.

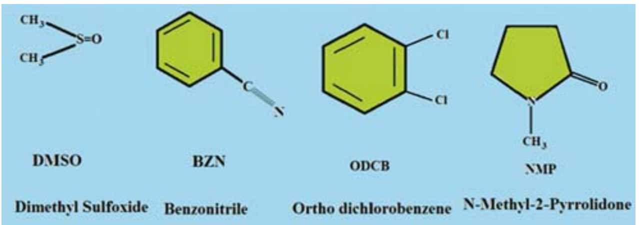

Fig. 15 — Molecular structures of common organic solvents used for graphene liquid phase exfoliation.

Fig. 16 — Stable graphene dispersions in acetone, pyridine, DMA, DMSO, ODCB, BNBZ, BA ,NMP and DMF organic solvents.

organic solvent ortho-dichlorobenzene (ODCB). Figure 14(a) shows the UV-Vis spectra of graphene dispersion obtained in ODCB after adding different organic salts. From these UV-vis spectra graphene concentration was calculated after applying the Lambert Beer's law and the resultant concentration is shown in Fig. 14(b). From this we observe that the maximum graphene concentration was obtained by adding edetate disodium (ED) salt in ODCB solvent.

It has been found that those solvents which have molecular structures similar to hexagonal benzene structure of graphene exhibited maximum increase in graphene concentration upon sonication. The molecular structures of common organic solvents DMSO, BZN, ODCB and NMP are shown in Fig. 15. The graphene dispersion in these solvents is found to be stable for two weeks as shown in Fig. 16. It shows stable graphene dispersions in acetone, pyridine, di-methylacetamide (DMA), dimethylsulfoxide (DMSO), ortho-dichlorobenzene (ODCB), benzylbenzoate (BNBZ), benzyl alcohol (BA), n-methyl-2-pyrrolidone (NMP), N,N- dimethylformamide (DMF) organic solvents.

In addition to organic solvents, some organic reagents have been utilized for exfoliation of graphene. An equimolar mixture of benzene hexafluorobenzene (C_6H_6–C_6F_6) has been reported by Oyer *et al.*[109] for the exfoliation of graphene. Because of the high affinity between the graphene nanosheets and solvent molecules, molecules assemble on both sides of the graphene nanosheets and helps in exfoliation. Benzene-hexafluorobenzene mixture can be used to obtain stable graphene dispersion of 50 mg ml^{-1} with a mild sonication. Because the boiling point of this mixed solvent is 78^{o} C, it can be easily evaporated after the formation of graphene layers on the desired substrate.

10 Electrochemical Exfoliation of Graphene

Recently graphene exfoliation has been done in ionic liquids, acids and various aqueous electrolytes through electrochemical route. The advantage of this method is the short time required for the exfoliation process and high quality of graphene produced.

In the electrochemical synthesis method a graphite rod acts as anode and platinum wire acts as cathode in the electrolyte solution as shown in Fig. 17(a). Figure 17(b) shows the actual experimental setup used to prepare graphene via electrochemical method. In some experiments graphite rods are used as both as anode and cathode. Upon applying appropriate DC voltage the exfoliation starts and the graphene nanosheets get dispersed in the electrolyte solution, which can be filtered and washed to get the pure graphene.

It has been reported by Loh *et al.*[110] that Ionic liquid [BMIM][BF_4] can be used as electrolyte for the electrochemical exfoliation of HOPG graphite. Through this electrochemical exfoliation process we can obtain graphene nanosheets of lateral size of few nm to µm size. Some of the aqueous electrolytes that have been used for graphene exfoliation are sulfuric acid, phosphoric acid, sodium sulphate, potassium sulphate etc. Various electrolytes that have been used for the electrochemical exfoliation of graphene along with the exfoliation time and the voltage required are listed in Table 3.

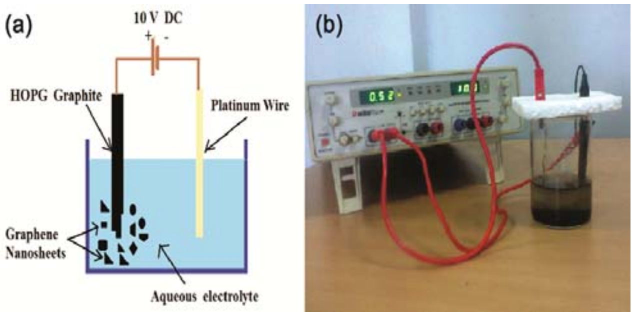

Fig. 17 — (a) Schematic diagram showing electrochemical exfoliation of graphene with platinum wire as cathode and graphite rod as anode and (b) actual experimental set-up used for electrochemical exfoliation of graphene.

Table 3 — Comparison of various electrolytes used for electrochemical exfoliation of graphene.

Aqueous electrolyte	Electrolyte concentration	Applied DC voltage	Exfoliation time	Exfoliation results
Ammonium chloride	0.1 M	10 V	5-10 min	No exfoliation
Sodium sulfate	0.1 M	10 V	3-5 min	Good exfoliation
Sodium nitrate	0.1 M	10 V	5-10 min	Poor exfoliation
Potassium sulfate	0.1 M	10 V	3-5 min	Good exfoliation
Sodium perchlorate	0.1 M	10 V	5-10 min	No exfoliation
Ammonium sulphate	0.1 M	10 V	5-10 min	Good exfoliation
Sulfuric acid	0.1 M	10 V	5-10 min	Good exfoliation
Phosphoric acid	0.1 M	10 V	5-10 min	Good exfoliation

11 Conclusions and Future Prospects

Liquid-phase exfoliation of graphite into graphene is a facile, easy and economical method for obtaining high quality defect-free graphene nanosheets. This method can be performed using the equipments easily available in the laboratories. The molecule of the solvent helps to overcome the Van der Waals force of attraction between individual graphene layers of graphite. It helps in the preparation of stable graphene inks which are used for making thin films and graphene composite materials.

In this review we have described the various liquids and solvents in which graphene can be exfoliated using sonication process.

However, the disadvantage of this method is low graphene concentration obtained which is usually less than 0.01 mg/mL. In order to improve the yield of liquid phase exfoliation, sonication time has to be increased from few hours to many days. As the sonication time increases the size of the graphene nanosheets reduces. Because of the variation in the parameters like ultrasonic power and time, temperature the final concentration of graphene and lateral size of graphene nanosheets also changes.

So, there is a need of a uniform protocol for the liquid phase exfoliation process. It is found that the molecules for enhancing graphene concentration should have high affinity for the basal plane of graphene, so that exfoliation can be enhanced.

So, the main research area is to explore those surfactants and concentration-enhancing agents which have high affinity towards the basal plane of graphene. Recently, significant research has been done to prepare high-quality pristine graphene through liquid phase exfoliation process for various applications. Usually, most of the exfoliating media used for liquid phase exfoliation method are expensive and have high boiling point. Surfactants used to prepare graphene in water are difficult to remove from the individual graphene nanosheets. The sonication process can decrease the size of graphene sheets if the process is continued for a significantly long time period. So, the main challenge is to select the right solvent for liquid phase exfoliation and proper electrolyte for electrochemical exfoliation method. The solvent and electrolyte chosen should be easily available, economical and it should be easily removed after the exfoliation process. For improving the graphene exfoliation, yield research should be directed towards the selection of new solvents having higher affinity for the graphene basal plane. It will enhance the liquid phase exfoliation process and increase the average size of the graphene nanosheets.

Besides the advantages of liquid-phase exfoliation method in comparison to other synthesis methods it can be improved if its properties are modulated by fictionalization via wet chemical route. It has been proved experimentally that fictionalization improves the electronic and chemical properties of graphene, which will make it more suitable for better electronic device applications. Therefore, it is hoped that in the near future research work should be concentrated on understanding of functional parts and then designing of desired materials. By doing this a precise control of the graphene properties will result in the use of graphene in advanced applications.

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