Supercritical Fluid Processing of Graphene and Graphene Oxide

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1. Introduction

Graphene which is single or few atomic layer carbon atoms in a hexagonal network is emerging as a leader among the 2D nanoscale materials [1]. Structurally, graphene is free of defects, with all the carbon atoms linked together by strong and flexible bonds. This has made graphene to have unusual electronic, optical, mechanical and thermal properties. The outstanding properties of graphene reported so far includes Young’s modulus (~1100Gpa), fracture strength (125 Gpa), high thermal conductivity (~ 5000 W m⁻¹K⁻¹), quantum Hall effect at room temperature [2–4], an ambipolar electric field effect along with ballistic conduction of charge carriers [5], tunable band gap and so on. Many efforts have been made on the preparation of the graphene via a number of physical and chemical methods. Some of these methods provides high quality graphene and has opened up new possible routes to address the challenges in preparation and molecular engineering of high quality processable graphene at low cost and large scale [4]. In spite of this progress, the standard procedure to make the high quality graphene is micromechanical cleavage method, which is suitable for only fundamental studies [3]. Alternatively, selective epitaxial growth of graphene on metal or nonmetal substrates using chemical vapor deposition or by thermal decomposition of SiC was developed [6]. The graphene-type carbon materials have been produced by substrate free CVD and radio-frequency plasma-enhanced CVD and so on [7]. On the other hand, the chemical routes are widely considered as a promising approach for large scale production [8]. This approach provides processable graphene, that can be easily cast into various structures or integrate graphene with other materials to form nanocomposites [8, 9]. Currently, there are two most popular chemical approaches to obtain graphene: dispersion and exfoliation of graphite/graphene oxide/graphite intercalation compounds and its reduction after exfoliation or direct exfoliation without chemical modification in suitable organic solvents or surfactants [8]. Unlike the direct exfoliation approach, the chemical modification method results in considerable destruction of graphene electronic structure, thus compromising its unique properties [10, 11]. In addition, these methods involve several steps and need 3-5 days to allow the intercalants and organic solvents to fully insert into the graphitic layers [12].

In contrast to this oxidation and reduction method, some people have developed direct graphite exfoliation method using suitable organic solvent. A high quality single layer graphene sheets (GS) have been prepared by the chemical solution process in which graphite was directly exfoliated in an organic solvent such as N-methylpyrrolidone (NMP)
under mild sonication [13]. In this work Coleman and co-workers have demonstrated that it is possible to effectively exfoliate graphite to produce single and few-layer GSs without the use of intercalants. The key to this success was the proper solvents for which the solvent–graphene interfacial interaction energy matches that of graphene–graphene. This method could produce a stable dispersion of graphene with the concentration of ~0.01mg/ml with a monolayer yield of ~1 wt%. This monolayer yield could potentially be improved to ~7-12 wt% with further processing. This approach resulted in the high quality graphene without any defects or oxides on the surface, which was completely different from that of the other solution method such as, graphite oxidation and reduction approach. Later, same group has developed a method to disperse and exfoliate graphite to give graphene suspended in water-surfactant solutions [14]. By Transmission electron microscopy, they had confirmed that the dispersed phase was mainly consisting of small graphitic flakes, in which more than 40% of these flakes had <5 layers with ~3% of flakes consisting of monolayer. Atomic resolution transmission electron microscopy shows the monolayer to be generally free of defects. The dispersed graphitic flakes are stabilized against the aggregation by Coulomb repulsion due to the adsorbed surfactant.

Few researchers have reported an environment-friendly method to produce graphene. For example, Loh et al. presented a green approach for reduction of graphite oxide to graphene using hydrothermal dehydration method [15]. Zheng et al. has reported solvothermal route to prepare graphene by direct exfoliation using oleylamine as a solvent as well as stabilizing agent [16]. Nuvoli et al has used a commercial ionic liquid 1-hexyl-3-methylimidazolium hexafluorophosphate (HMIH), as a convenient solvent medium for graphite exfoliation in mild and easy conditions without any chemical modification [17]. This method resulted in few layer graphene with a concentration as high as 5.33 mg/ml, which is the highest value reported so far in any solvent. However, most of these methods take long reaction time and some time they need size separation process in order to remove unexfoliated large graphite flakes.

On the other hand, the supercritical fluids (SCFs) have been widely studied as a new kind of reaction media for nanomaterials synthesis owing to their unique properties such as; gas like diffusivity, low viscosity and the density closer to that of liquid [18-20]. The SCFs have much more empty space than ordinary liquids and are highly compressible. Consequently, the density and hence “the solvent strength” of the fluid may be tuned from “gas-like” to “liquid-like” values simply by varying pressure, temperature, or both. This tunability, along with low interfacial tension, excellent wetting of surfaces, and high diffusion coefficients, makes supercritical fluids potentially superior solvent for diffusion in between the layers and its expansion. Taking advantage of these unique properties of SCFs, recently, we have developed a novel SCF method for the exfoliation of graphite to obtain the high quality and high yielding graphene sheets [18]. This rapid and facile one-pot exfoliation method resulted in highly conductive GS maintaining its original nature, although a high temperature and pressure were used to create a suitable environment for SCF exfoliation. Direct high-yield conversion of graphite crystals to GS was possible under SCF conditions because of the high diffusivity and solvating power of SCFs, such as ethanol, N-methylpyrrolidone (NMP), and DMF.

Currently, the focus has been shifted considering the graphene as ideal 2D materials to understand the fundamental physics to its treatment as a large carbon macromolecule which offers new promise [21]. Years of research on carbon nanotube, fullerene, and graphite have produced a myriad of chemical pathways for modifying sp² carbon structures, which will undoubtedly be adapted to functionalize both the basal plane of graphene and its reactive
edges. This not only promises to deliver handles for exploiting graphene’s intrinsic properties but also should lead to new properties altogether. Interaction of graphene with electron-donor and electron acceptor molecules causes marked changes in the electronic structure and properties of graphene [24, 25]. Thus, electron donor molecules, such as aniline and tetrathiafulvalene (TTF), soften (i.e. shift to lower frequency) the Raman G band of few-layer graphene while electron-acceptor molecules, such as nitrobenzene and tetracyanoethylene (TCNE), stiffen (i.e. shift to higher frequency) the G band. As demonstrated by Subrahmanyam et al. the graphene can be functionalized through noncovalent modification without affecting its electronic structure by wrapping with surfactants or through π-π interaction with a pyrene derivative such as 1-pyrenebutanoic acid succinimidyl ester (PYBS). Recently, we have reported the SCF exfoliation and surface modification of graphene using 1-PSA molecules [30]. The π-π interaction between the graphene layer and aromatic ring of modifier molecules resulted in the modifier-graphene composite without any damages to the graphene surface and its electronic conductivity under SCF conditions.

In the present work, we have found that methanol, which is cheaper solvent than that were used in our previous report can also be effective in exfoliation of graphite. This can also yield a high quality and large scale graphene solution, which are stable for several days without any surfactant. In this chapter, we highlight the structural and molecular engineering of graphene and GO by exfoliation, chemical functionalization, and reduction under SCFs. Such structural and molecular engineering of graphene under SCFs plays a crucial role in retaining and restoring the original properties of the resulting graphene sheets. We present the detailed study of the role of SCFs conditions on the exfoliation, covalent and non-covalent functionalization and GO reduction in one pot process. The solvent and molecular engineering under SCFs is of great interest because it enables the attachment of suitable organic molecules through π-π interaction. In this chapter, we are presenting a comparative study on SCF process over other methods that have been used for the exfoliation, surface modification and GO reduction. The different reaction conditions such as type of SCF, reaction time, temperature, solvents and organic molecules ratio had the significant effect on the exfoliation and surface modification of the graphene. We have also noticed the influence of some reaction conditions on the structure and electronic properties of the graphene or reduced GO.

2. Experimental section

2.1 Preparation of graphene by supercritical methanol

The preparation of graphene by supercritical methanol was similar to that reported in our previous study. First we pretreated graphite flakes with dilute sulphuric acid and nitric acid. The exfoliations were performed in a stainless steel reactor having a maximum volume of 10 ml. In a typical experiment, 30 mg of pre-treated graphite crystals were taken in a stainless steel reactor vessel and dispersed in 5 ml methanol by low power sonication (AS ONE US cleaner, US-4R, 40kHz, 160 W) for 10-minutes. Then, the sealed reactor vessel was heated up to 300-400 °C for 30-60 minutes in a special designed tube furnace (AKICO, Japan). The reactor reaches optimum temperature within the 3 minutes, therefore, the reaction time mentioned above includes ramp up time. The pressure was maintained at 38-40 MPa by adjusting the volume and temperature of the reactor vessel. The reaction was terminated by submerging the hot reactor in an ice-cold water bath. The exfoliated GS were collected by repeatedly washing and centrifuging with fresh solvents and vacuum dried over night at 100 °C.
2.2 Material characterization
Exfoliated GS were confirmed by measuring the Raman spectra in the regions of G and 2D bands using a NIHON BUNKO Ventuno spectrometer (NSR-1000DT). In case of 2D band observations, for each sample 105 spots were measured from 3 different regions with regular spacing to count the number of layers. The G band of monolayer in each sample was recorded after confirming monolayer spot from the 2D band spectra. The high resolution transmission electron microscopy (TEM) observations were carried out by a JEOL JEM-2101F with an operating voltage of 200 kV. The TEM samples were prepared by dropping the solution of each samples dispersed in ethanol onto carbon holy grid (JEOL, 400 meshes). Fourier transform infrared spectroscopy (FT-IR) results were recorded on a FT/IR-6200 IR spectrophotometer (JASCO Corp., Tokyo, Japan). The atomic force microscopy (AFM) measurements were performed with S-image, Multi-Function unit. Graphene suspensions were applied directly on the substrate, which is a thin native oxide on Si (100), by drop casting method. After drying the substrate in a clean environment at room temperature, the measurements were performed in air at ambient temperature and pressure.

3. Results and discussions
It is well known that the surface energy of solvents matching with that of graphene will help to exfoliate graphite directly to obtain graphene [13]. However, in our previous study we have demonstrated that a rapid and high yield graphite exfoliation can be carried out using SCFs such as DMF, NMP and ethanol due to their unique properties [18]. Presently, we found that cheaper solvent methanol also can be effective as supercritical solvent in order to obtain a high quality and high yield graphene. The graphite pretreatment with acid facilitates the dispersion of graphite flakes in methanol under ultrasonic treatment. Then the graphite exfoliation under supercritical methanol (SCM) occurs due to the low interfacial tension, excellent wetting of the surfaces and high diffusion coefficient of SCM. Because of these properties, the SCM solvent molecules can rapidly penetrate through the inter layers of graphite with high diffusivity and solvation power, which is much higher than the interlayer energies of graphite. This resulted in a rapid and high yield conversion of the starting graphite crystals down to 1-10 layers GS, retaining the original pristine structure of the sheets in one pot exfoliation. Figure 1 shows the schematic illustration of simple SCM exfoliation of pretreated graphite flake to form GS.

![SC methanol exfoliation](image)

**Fig. 1.** Schematic illustration of the supercritical fluid exfoliation of graphite flakes into graphene sheets.
The prepared sheets were characterized by the Raman spectroscopy, atomic force microscopy (AFM) and high resolution transmission electron microscopy (HRTEM) to confirm the formation of GS. The Raman spectroscopy and AFM both are the powerful non-destructive techniques for precisely identifying the number of graphene layers and structure of graphene.

Figure 2 shows the AFM image and height profile of GS. The formation of monolayer graphene was confirmed by measuring a AFM height profile of the single GS deposited on the silicon substrate. Figure 2 shows the representative AFM profiles measured for monolayer graphene. This height profile shows the steps from the Si substrate to an exfoliated sheet, which is about 0.8-0.9 nm for given cross-section (A-B). A typical solution process based single-layer sheet shows the step heights of ~0.6-1 nm under AFM and was well documented by several researchers in the literature [13-14]. For example, Hernandez et al. had observed number of thinner objects with typical height of 1-2 nm under AFM as monolayer, which was exfoliated by sonication. They attributed this large thickness of the monolayer to the chemical contrast issues and the presence of residual solvent. Since our sample also contains some residual solvent, similar thickness can be expected for monolayer rather than the ideal thickness (0.3 nm) reported by some other methods. We have also observed the thickness corresponding to 3-10 layers of GS, similar to the samples that were obtained by other supercritical solvents such as NMP, DMF and ethanol. However, in the present study it was realized that, quite often the graphene layers were overlapping each other as AFM specimens were prepared by drop-casting the dispersion of the GS on a smooth substrate surface.

Fig. 2. AFM image of graphene nanosheets obtained from SC Methanol process 60 min reaction time at 400 °C.

In order to confirm the high yield exfoliation of graphene, we have measured the Raman spectra for exfoliated samples. The Raman spectra was recorded over the 210 spots from 4 different regions of the sample mounted on a glass slide to confirm the yield and count the number of layers. The total area subjected for the measurement was 1500 μm². The Raman spectra was recorded with a red (633 nm) laser radiation using the dried powder mounted on the glass slide. The typical D (1350 cm⁻¹), G (1565 cm⁻¹) and 2D (2650-2690 cm⁻¹) graphitic bands are present in the spectra of all the exfoliated samples. We observed the ‘D’ and ‘G’ bands at ~1332 cm⁻¹ and 1581 cm⁻¹ respectively. Presence of a small ‘D’ band in our starting graphite crystals indicates that they already had small defects. The ‘D’ band intensity was slightly increased for the exfoliated GS samples. Relatively small increase in the ‘D’ band intensity of GS samples indicates that exfoliated GS samples have a less or no defects.
Hernandez et al. also reported a small ‘D’ band in their samples, which were prepared by dispersing graphite in different organic solvents such as NMP under sonication. The Raman spectra recorded in 2650-2690 cm$^{-1}$ (2D band) region for all the samples is presented in Figure 3b. We could precisely identify the number of layers from the shape and position of the 2D band. The spectra Raman spectra indicate that the sample consists of single to few layer graphene (1-5). The Raman spectra of our samples agreed well with the literature [22-23]. The estimated yield of exfoliated graphene by Raman spectra about 90 %. Among the observed GS majority of sheets were < 5 layers. This result indicate the high yield exfoliation of graphite crystals to few layer GS under SCM conditions.

Fig. 3. Raman Spectra of D, G and 2D band region of graphene nanosheets prepared at 400°C for 60 min reaction.

Fig. 4. TEM images of exfoliated graphene nanosheets; a) mono and multi layer graphene sheets, b) portion of large graphene sheets with some mono-trilayer sheets at the left corner.
The morphology and size of the obtained sheets were confirmed by HRTEM observation. The ability to easily transfer GS on to the TEM grid allows their detailed characterization using HR-TEM. The TEM samples were prepared by simply dropping few drops of dispersed solution on to holey carbon grids (400 mesh). TEM analysis revealed a large quantity of sheets with different types and sizes as shown in Figure 4. The size of the GS was in the range of several hundred nanometers to 1 micrometers. Most of the GS are agglomerated comprising from mono to multi layer sheets as displayed in Figure 4 and some of them are only mono layer GS. From TEM images we can notice that our GS has a wavy like texture and rolled up at the one end. Large flakes were not observed in our samples. It should be noted that in the present method, we did not employ any flake separation by centrifugation. These TEM images are in consistent with Raman analysis that is the large proportion of sheet is < 8 layers.

4. Functionalization of graphene sheets

Graphene has been functionalized by both covalent and noncovalent means to disperse or solubilize them in different solvents [24]. Generally, covalent functionalization of graphene is carried out with a long-chain alkyl amide, accomplished by acid treatment followed by reaction with thionylchloride and dodecylamine [25-26]. Amide-functionalized graphene is soluble in organic solvents such as tetrahydrofuran (THF), carbon tetrachloride (CCl4) and dichloromethane (DCM) [27]. Graphene is also functionalized by interaction with organosilane and organotin reagents such as hexadecyltrimethoxysilane (HDTMS) and dibutylidimethoxytin in order to obtain the stable dispersion in organic solution. Treatment of graphene with a mixture of H2SO4 and HNO3 makes graphene dispersion stable in water. Similarly, we can obtain water soluble graphene by sulfonation and electrostatic stabilization. Non-covalent functionalization of graphene also been reported by employing different methods such as wrapping with polyethylene glycol (PEG) and other surfactants, or π-π interaction with a pyrene derivative such as 1-pyrenebutanoic acid succinimidyl ester (PYBS) [25-29]. Advantage of non-covalent functionalization is that surface can be modified without affecting its electronic structure [27, 29]. Wrapping with PEG gives water-soluble graphene. By π-π interaction with PYBS, graphene becomes soluble in dimethylformamide. The figure 5, shows the schematic illustration of direct graphite exfoliation and functionalization using organic molecules.

![Schematic Illustration of Graphene Sheet Functionalization](image-url)
SCF is one of the potential reaction media for carrying out the graphene functionalization. Introduction of surfactant molecules during the SCF exfoliation could result in the homogeneously modified GS. As surfactant molecules are miscible with SCF and diffuse through the layers of graphite along with SCF, the graphite exfoliation and surface modification can be carried out simultaneously in a one pot process. Some researchers already have demonstrated that when the surfactant molecules with aromatic rings were chosen as a modifier, the \( \pi-\pi \) interaction between the graphene layer and aromatic ring of modifier molecules can result in the modifier-graphene composite without any damages to the graphene surface and its electronic conductivity. Recently, we have demonstrated the 1-pyrene sulfonic acid sodium salts (1-PSAs) modified GS by the novel one-pot in-situ SCF exfoliation and modification reaction using the mixture of ethanol and water as solvent [30]. The 1-PSAs molecules on the surface of graphene layers acted as electron withdrawing group resulting in an electron transfer from GS surface to 1-PSA molecules. This was confirmed by the Raman spectra.

We also confirmed similar surface functionalization of graphene using SCM conditions. The 1-PSA molecule functionalization was also successful under the SCM conditions. This was confirmed by a red shift from 1572 cm\(^{-1}\) ~ 1576 cm\(^{-1}\), in the graphitic ‘G’ band of the Raman spectra. Figure 6 shows the red shift in G band of Raman spectra. SCF process is suitable for functionalization of graphene with various functional molecules through covalent or non covalent molecular engineering on the surface.

![Fig. 6. Raman Spectra of G band region of as prepared and functionalized graphene nanosheets.](image-url)

The surface nature and functionality of 1-PSAs modified sample was confirmed by IR measurement. The figure 7 shows the typical IR spectrum of graphite and 1PSAs modified graphene. A weak vibration mode at \(~3400\) cm\(^{-1}\) reflects that a few hydroxyl groups are present on the edge and/or defect site of graphite. Whereas, the vibration modes of the hydroxyl group and sulfonic acid group were observed around \(~3400\) cm\(^{-1}\) and \(~1180\) cm\(^{-1}\).
respectively, for 1-PSAs modified sample (fig 7b). The appeared hydroxyl band at ~3400 cm$^{-1}$ can be attributed to the -OH group in sulfonic acid, which was substituted with sodium ions during the exfoliation process. The small amount of defects that is already present in the starting graphite material along with the defect induced by a mild acidic environment can be expected in this work. Although IR spectroscopy is not quantitative analysis method, it is expected that a fraction of R-SO$_3$H per -OH will be increased linearly with an increase in the concentration of 1-PSAs molecules. As we estimated in our previous study, a linear slope was obtained by plotting the peak height of R-SO$_3$H per -OH vs. 1-PSAs concentration in the starting solution [30]. This work shows a systematic fabrication of 1-PSAs modified graphene nanosheets (imGNSs) with different ratios of the sulfonic group on the GS surface is possible using various supercritical solvent such as methanol, ethanol, NMP, DMF and so on.

![Fig. 7. FTIR spectra of starting graphite and graphene sheets functionalized with 1PSAs under supercritical fluid conditions.](image)

5. Graphene oxide reduction under supercritical fluid

Preparation of graphene by the chemical reduction approach is one of the most popular and favorable, because it can be scalable in production and is versatile in realizing abundant chemical functionalization [8,9]. Ruoff et al. first observed that homogeneous colloidal suspensions of electrically conducting graphene could be produced via the chemical reduction of GO with dimethylhydrazine or hydrazine, in the presence of either a polymer or a surfactant [9]. This line of research opened new avenues for the production of graphene using chemical methods. Different homogeneous colloidal suspensions of graphene have been successfully prepared by some groups. For example, Li et al. demonstrated that aqueous graphene dispersions were readily formed by controlled chemical conversion of GO colloids through electrostatic stabilization [31, 33]. Dai et al. successfully produced...
Graphene nanoribbons with a width of <10 nm by sonicating the expandable graphite after thermal exfoliation [32]. Yang and Kaner et al. obtained large-scale graphene by reducing GO in pure hydrazine [34]. However, major drawback of this approach is the Hydrazine, which is highly toxic and unfortunately, the use of highly toxic and dangerously unstable hydrazine or dimethylhydrazine to reduce GO requires great care. In addition, this route takes longer reaction time and multiple steps to obtain the reduced GO. Therefore, there is an increasing demand to find nontoxic and effective approaches for chemically producing graphene, which can also be easily scaled up. Few successful attempts to develop the environmentally-friendly methods to produce graphene have been reported. For example, Loh et al. presented a “green” reduction of GO to graphene using hydrothermal dehydration [15]. Recently, Zhang et al have reported an environment-friendly method to produce graphene that employs Vitamin C as the reductant and amino acid as the stabilizer [16, 35]. This study is the first example of the use of biocompounds for nontoxic and scalable production of graphene. Followed by this work, Dong et al has reported another green and facile approach to the synthesis of chemically converted graphene nanosheets (GNS) based on reducing sugars, such as glucose, fructose and sucrose using exfoliated GO as the precursor [36]. The graphene produced by these methods shows the similar electrical properties that are produced by other methods. However, in most of these reduction cases the structural defect of graphene is not completely restored.

In this regard, we have employed the SCF process for the reduction of GO using ascorbic acid or sugar as reducing agent under SCF conditions. First, we prepared GO by using the Hammers method for which the procedure is reported elsewhere [8]. About 20 mg of the dried graphene oxide powder was dispersed in 5 ml ethanol. Then, to this solution we added about 0.5-1 ml aqueous solution containing 1 mg ascorbic acid or sugar. The solution was mixed well under 1-2 min sonication. Then the solution was transferred to the stainless steel reactor and heated up to 300°C for 10-15 min at 30-38 MPa. After the reaction, reactor was quenched with ice cold water and samples were collected by centrifugation followed by drying at 100°C. For comparison, we also prepared reduced graphene by using hydrazine as reducing agent reported in literature.

Fig. 8. Schematic illustration of the reduction of graphene oxide to graphene sheets under supercritical fluid conditions.

The structural and electronic properties of all the reduced GO were studied by Raman spectroscopy as it is one of the most widely used techniques to characterize the structural and electronic properties of graphene, including disorder and defect structures, defect density, and doping levels. Generally, the Raman spectrum of graphene is characterized by two main features, the G mode arising from the first order scattering of the E2g phonon of sp² C atoms (at ~1575 cm⁻¹) and the D mode arising from a breathing mode of k-point photons of A1g symmetry (~1350 cm⁻¹) [37]. Therefore, we have compared the D and G band of SCF reduced
GO that with hydrazine reduced GO. Figure 9 shows the Raman spectra of GO and SCF reduced GO. From the Raman data we can observe that in the GO, the G band is broadened and blue shifts to 1591 cm\(^{-1}\) due to the presence of isolated double bonds that resonate at higher frequencies than the G band of graphite [37, 38]. In addition, the D band at 1330 cm\(^{-1}\) becomes prominent, indicating the reduction in size of the in-plane sp\(^2\) domains due to the extensive oxidation. After its reduction under SCF with ascorbic acid, the Raman spectrum of as-prepared GS also exhibits a weak D band and strong D at 1326 and 1576 cm\(^{-1}\), respectively (Figure 9b). It should be noted that the frequency of the G and D bands in the SCF reduced GO is close to that of graphite, when compared to the as prepared GO. However, the increase in the D/G intensity ratio, compared to pristine graphite, indicates a decrease in the size of the in-plane sp\(^2\) domains and a partially ordered crystal structure of the GS [38]. In contrast, the intensity ratio of reduced GO by hydrazine is more close to as prepared GO, when compared with our results. These results suggest that the quality of SCF reduced GO is better than any other method as SCF method facilitates the restoration of original graphene structure due to high pressure and temperature and unique SCF properties.

![Raman spectra of D and G band regions](image)

**Fig. 9.** Raman spectra of D and G band regions; (a) graphene oxide, (b) graphene oxide reduced by SCF.

Further, we compared the structural properties of our SCF reduced GO by studying the powder X-ray diffraction patterns. Figure 10a shows the XRD patterns of the pristine graphite, GO and SCF reduced GO. The characteristic reflection (002) of all the samples can be compared in order to understand the structural changes before and after the reduction. Pristine graphite shows a strong intensity peak for reflection (002), whereas, the graphite oxide shows the broad peak due to disorder with peak shift (data not shown). In contrast to this, the GO reduced by hydrazine shows a low intensity peak for (002). Whereas, SCF reduced GO shows a relatively good (002) reflection. A slight shift in the peak position and d-spacing of characteristic reflection (002) indicates that the reduced GO have restored the original pristine structure after the SCF reduction, when compared to GO reduced by hydrazine. This is evidenced in the figure 10b and c.
6. Conclusion

In summary, we have successfully demonstrated the potential application of SCFs as reaction medium for the exfoliation, surface modification and reduction of GO to high quality graphene in one-pot and rapid supercritical fluid method. We have introduced cheaper solvent methanol, as novel SCF for graphite exfoliation as well as for molecular engineering of GO and graphene to restore its original structural and electronic properties. In-situ surface functionalization of graphene under SCF gives efficient route to alter the electronic properties of GS. The SCF reduction of GO to GS shows a promising way of restoring original structure of graphene. The comparative analysis of hydrazine reduced GO and SCF reduced GO shows restoration of G band in the Raman spectra and (002) reflection in the XRD patterns. This result indicates that SCF process is very effective method among any other solution route to produce high quality GO reduced graphene.

Fig. 10. XRD patterns of (a) graphite, oxidized graphite and supercritical fluid reduced graphene oxide, (b) hydrazine reduced graphite oxide and supercritical fluid reduced graphene oxide and (c) graphite and supercritical fluid reduced graphene oxide showing the peak shift after reduction.
7. Acknowledgment

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8. References

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The discovery of graphene has led to a deluge of international research interest, and this new material in the field of materials science and condensed-matter physics has revealed a cornucopia of new physics and potential applications. This collection gives a roughly review on the recent progress on the synthesis, characterization, properties and applications of graphene, providing useful information for researchers interested in this area.

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