CHAPTER - 7

Conclusion and Scope of Future Work

7.1. Conclusion

Good physical, mechanical properties, thermal and electrical properties make graphene as leading material for future applications. It became subject of interest for researchers to explore and utilize its properties for various applications ranging from civil, defense to aerospace and electronics applications etc. High strength and modulus of graphene promises its application for structural composite reinforcement. High surface area of graphene is also favourable for it is being utilized as reinforcement. Lot of research has been done to discover physical properties of graphene. It includes semiconducting behaviour, thermal conductivity, electrical conductivity and some fundamental research related to basic theory of physics. Fabrication techniques of alone single-layer graphene sheet have been developed by various groups. Comparatively less work has been done to demonstrate graphene as reinforcement for composite fabrication for structural and other applications. It needs development of sounding method for synthesis of graphene sheets in bulk amount. The work carried out under present studies are compiled in the thesis was with aim to use simple chemical route to synthesize graphene oxide in bulk form and use it for making polymer matrix and carbon matrix composites.

Bulk Graphite has been used as raw material for synthesis of graphene. Chemical
oxidation method was used for synthesis of graphite oxide (GO) from natural graphite. Graphite oxide is one of the base sources of graphene like material for mass production. Various kinds of exfoliation techniques have been used to separate graphene planes apart from each other. Raw materials were characterized by various techniques like silica and Fe content, particle size distribution, XRD analysis and FTIR analysis. Raw materials were subjected to cleaning for removal of impurities like silica and Fe. Graphite was washed by HF and again analyzed for silica and Fe content. XRD and FTIR analysis shows good orientation of graphite flakes with presence of some functional groups attached to graphitic planes.

In the very beginning, Modified Hummer’s Method was used to synthesize graphite oxide followed by exfoliation by ultrasonication of Graphite oxide to get dispersion of oxygen functionalized graphene oxide in water (GO). Graphite oxide was synthesized in two steps: pre oxidation of natural graphite followed by full oxidation of pre oxidized graphite. Acid mixture of $\text{H}_2\text{SO}_4$ with $\text{K}_2\text{S}_2\text{O}_8$, $\text{P}_2\text{O}_5$ and $\text{KMnO}_4$ were used as intercalant or oxidant. Graphite oxide and dispersion of graphene oxide in water were characterized by various techniques. FTIR analysis shows increase in functionality as degree of oxidation increase. In this oxidation method mainly carboxylic groups, hydroxyl groups and phenolic groups were found to have got attached to graphene sheets. XRD analysis confirms significant increase in inter planer spacing of graphitic planes from 3.34 Å to 8.48 Å because of functional groups attached and also increased up to 9.13 Å after ultrasonication of GO. TEM analysis was carried out to observe changes in planer structure and planer stacking of graphene oxide. It was found that graphite oxide
(GO) is bunch of planes instead of single layer of graphene and after exfoliation it was in form of single to few layer graphene oxide.

Synthesis of graphene from dried graphene oxide paper was done by thermal exfoliation technique. Thermal exfoliation of Graphene oxide paper was carried out at low temperature 230°C as compared to 1000°C generally used by other researches. This low temperature technique can be used for mass production of graphene like material. Low temperature thermal exfoliation follows the same general mechanism as that for the high temperature case. This approach is facile, low cost and easy to be scaled up for mass production. DSC study of graphene oxide paper helps to optimize low temperature for exfoliation and that temperature is near to 230°C. XRD analysis shows absence of planer stacking of graphite oxide as well as graphene oxide paper showing complete exfoliation. TEM micrograph also gives support to the XRD results of exfoliated graphene. SAED patterns of samples before exfoliation of graphene oxide paper show long range ordering of graphene oxide sheets and after exfoliation only diffuse and weak rings appeared which indicate the loss of long range ordering between Graphene sheets.

BET specific surface area of exfoliated graphene sheets was determined to be 1283 m²/g which is much higher than surface area of dry Graphene oxide paper but is still lower than surface area of single layer graphene (is 2630 m²/g). Specific surface area of this exfoliated graphene was higher than that of graphene obtained at 1050°C (~700 m²/g) and also much higher than that of graphene obtained at 200°C under vacuum (~ 400 m²/g). Surface area of exfoliated sample was found to be about ~ 2.1 times lower than that of the ideal specific surface area (2630 m²/g) of a single graphene sheet, which indicates that each exfoliated platelet comprised of ~3 to 4 individual graphene sheets on
average. The FTIR results also showed simultaneous reduction of graphene oxide after exfoliation.

Flexible conductive graphene paper can be obtained through direct and gentle thermal annealing of parent graphene oxide paper and thermal annealing was carried out at 250°C under hydrogen atmosphere. Thermal treatments under argon or hydrogen atmosphere are shown to be highly efficient methods to improve the reduction of graphene oxide paper, leading to a significant removal of oxygen-containing functional groups and to an efficient recovery of the sp² network structure. The resulting graphene (i.e. TRGP) papers exhibit electrical conductivities up to 1.3 x 10² S/m that is 4 orders of magnitude higher than the original graphene oxide paper. The recovery of the electrical properties of the graphene paper after annealing in terms of an effective restoration of the sp² carbon network ensured reduction of the Graphene oxide paper, resulting in an increase of the charge carrier transport in individual graphene sheets.

Moreover, this direct thermal reduction treatment allows maintaining the structural integrity and mechanical flexibility of the parent graphene oxide paper after annealing. Our approach suggests an easy, cost effective and environmentally friendly fabrication route for flexible conducting graphene paper of great application potential as flexible electrodes in fields, such as energy storage/harvest (supercapacitors, batteries) and sensors.

Epoxy polymer composites were fabricated by loading various proportion of exfoliated graphene in epoxy resin. Adding 1.5 wt% of graphene to the epoxy matrix increases the glass transition temperature and maximum decomposition temperature of composites up to 139.6°C and 390.5°C respectively as compared to that of pure epoxy
matrix as 126.8°C and 341°C respectively. Increase in glass transition temperature of composites can be explained by two factors. First, graphene sheets confine polymer chains and reducing their mobility after introducing graphene into the matrix. It is believed that graphene can act as physical interlock points in the cured organic matrix, which generally not only provide a sterically hindered environment for curing reactions of composites but also restrains the chain mobility. Second, the matrix and chemical groups on the filler surface may participate in curing the reaction which leads to higher crosslinking density.

Tensile strength and young modulus of composites increased by 27% and 16% respectively for loading of 2 wt% of graphene. Upon higher loading of filler in composites the decrease in properties were observed. This is due to formation of agglomeration in composites which can be seen in SEM micrographs of fractured surfaces of composites. Graphene also affects the electrical conductivity of composites and increase in conductivity up to $10^{-1}$ S/m for the loading of 2.5 wt% graphene in epoxy matrix was observed which is much higher than pure epoxy.

Carbon based composites were fabricated by powder mixing method. Phenolic resin (Novolac type) mixed with 12 % hardener was used as the matrix precursor and 4 wt% Exfoliated graphene powder, CNTs and natural graphite flakes (NGF) were used as reinforcement in composite. Composites were heated at 1000°C for carbonization and at 2700°C for graphitization. Graphene shows excellent effect on graphitization and conductivity of composites as compared to CNTs and NGF. XRD and Raman results show graphene loaded composite more graphitic in nature after graphitization respect to CNTs and NGF loaded composites. XRD results show highly intense peak and G-band in
Raman spectra also shifted to position of pure graphitic nature for graphene reinforced composite. Graphene loaded composite shows higher conductivity because of formation of continuous network of graphene and matrix carbon in composite. The conductivity was found to $3.30 \times 10^2$ S/m with 4 wt% loading of exfoliated graphene in carbon composite.
7.2. **Scope of future work**

The present work comprises of synthesis of Graphene and development of composites using these. A good amount of work was done and important conclusions have been drawn. However, research is never ending task so more work can be done in future on following lines.

- Low temperature exfoliation method to be used for mass production of graphene like material for commercialization.
- Interaction of graphene with matrix material can be improved by tailor making changes in functionality.
- Utilization of exhaustive properties of graphene in composite with epoxy as well as other matrix systems can result in more interesting research.
- High mechanical properties can lead graphene for good choice as reinforcement in other composites like ceramics, metals etc. for structural applications.
- As being high surface area material graphene can be used as good absorbent for various materials in dry and dispersion form.
- Some changes with functionality can lead graphene as good candidate for gas storage applications.