Non-Destructive Synthesis and Characterisation of 1D Carbon Nanotubes and 2D graphene sheets for the Development of Nanocomposites

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Abstract

1D carbon nanotubes (CNTs) and 2D graphene nanosheets possessing extraordinary mechanical, thermal and electrical properties are tempting reinforcements for the fabrication of ultra-light, high strength and high efficiency metal-matrix composites (MMCs), ceramic-matrix composites (CMCs) and polymer matrix composites (PMCs). By the virtue of their unique structure, size, and shape, they exhibit distinct properties, beneficial for advanced nanocomposites used in structural and functional applications. A graphene nanosheet with ultimate strength of 130 GPa, Young's modulus of 1 TPa, is one of the strongest materials known. It possess a very high electric conductivity (~6000 S/cm), enormous specific area of (~2600 m^2/g) and a great thermal conductivity (~5000 W/mK). CNTs display tensile modulus of ~1 TPa and strength ~50–150 GPa with a failure strain more than 5%. Due to the existence of very large surface area and chemically active sp_2 and sp_3 hybridisation, the chemical bonding of these nanofillers is far different to other conventionally used 3D materials. Graphene is composed of sp_2 carbon structures arranged in a honeycomb lattice which could be wrapped into 0D fullerenes, rolled into 1D nanotubes or 3D graphite when a number of layers are stacked together. Traditional nanofillers usually include micron sized conventional reinforcements, which require very high loading levels to provide moderate enhancement in the properties of the composites, causing issues in the processing due to their high viscosity whereas, on the other hand, nanofillers in the range of 3vol. % to 5vol. % are capable to achieve the same mechanical properties as compared to 20 wt. % to 30wt. % of micron sized fillers. Thus, nanocomposites have a weight advantage over conventional composites and so nanofillers have emerged as the pleasing candidates for the fabrication purpose. Their increased specific area enables higher interfacial interactions and hence provide higher modulus. The present work describes the innovative non-destructive strategies to synthesize high performance 1D/2D materials. The comprehensive review of the processing routes, parameters and techniques used for the synthesis and characterisation of graphene and multiwalled carbon natubes (MWCNTS), which were later incorporated for the development of ceramic based nanocomposites has been illustrated. Nanosized graphene sheets were developed by the intercalation method and modified Hummers method. MWCNTs were processed and prepared by Low pressure chemical vapour deposition (LPCVD) technique. The influence of surface chemistry, processing techniques and functionalization of the nanofillers on the tribological morphology is highlighted. The microstructural characterisation of the nanofillers was done by Optical microscopy, X-ray Diffraction, Field Emission Scanning Electron Microscopy, High Resolution Transmission Electron Microscopy, Raman Spectroscopy, Fourier Transform Infrared Spectroscopy, Atomic Force Microscopy, X-ray Photoelectron Spectroscopy, Particle Size Analysis, Thermal analysis.

Keywords: Graphene, Carbon Nanotubes, MMCs, CMCs, PMCs, Intercalation, Hummers Method, LPCVD.

Non-Destructive Synthesis and Characterisation of 1D Carbon Nanotubes and 2D Graphene Sheets for the Development of Nanocomposites

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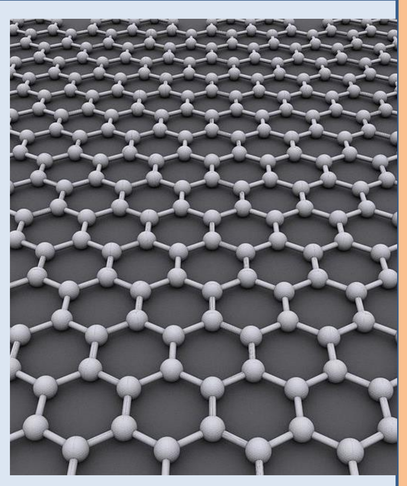
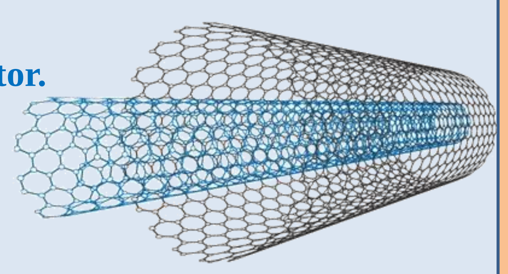
What is Graphene?



- 1 atom thick layer of graphite
  - Honeycomb (hexagonal) lattice
- It is the basic structural element of the other allotropes, including graphite, charcoal, CNTs and fullerenes.
- It is the strongest, thinnest material known to exist.

What is CNT?

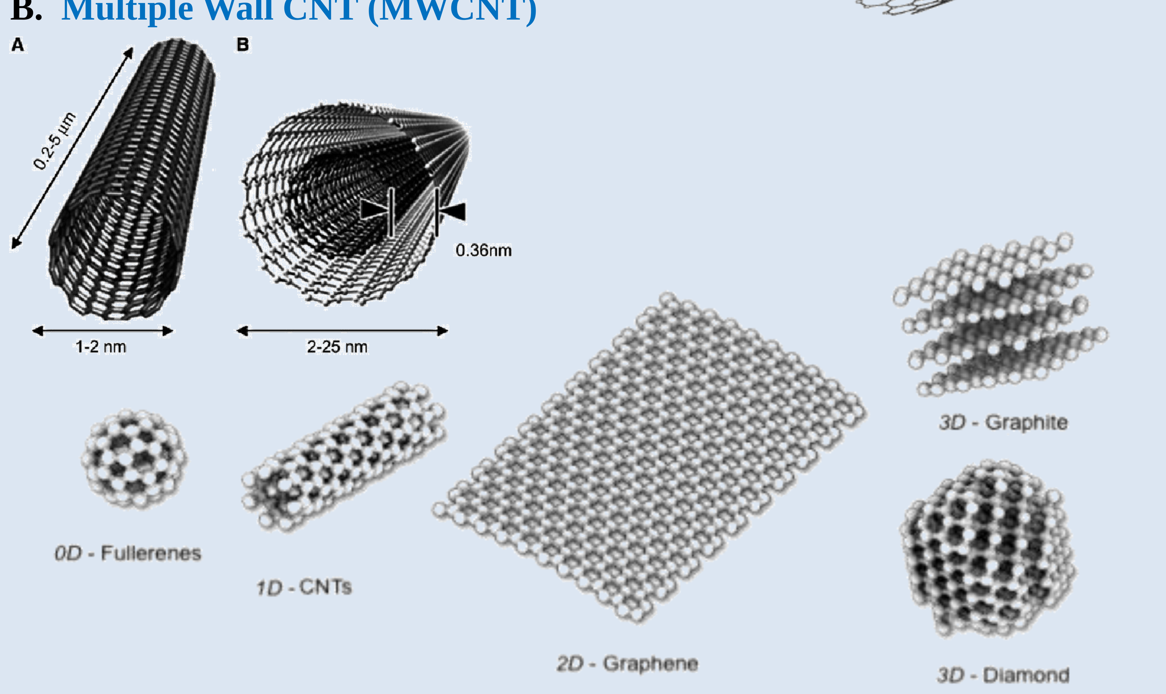
- CNT is a tubular form of carbon with diameter as small as 1nm. Length: few nm to microns.
- CNT is configurationally equivalent to a two dimensional graphene sheet rolled into a tube.
- A CNT is characterized by its Chiral Vector.



Types of CNTs

A. Single Wall CNT (SWCNT)

B. Multiple Wall CNT (MWCNT)



Synthesis of 2D Graphene

Intercalation of As-received Natural Flake Graphite
↓
Solvent Dispersion
↓
Formation Of GIC (Expanded Graphite)
(-Gr-H_2SO_4-Gr-Gr-Gr-Gr-H_2SO_4-Gr-Gr-Gr-)
↓
Thermal Exfoliation
↓
Sonication In Acetone For Four Different Time Spans (5,7,12,20 h) At Room Temperature
↓
Formation of xGnP

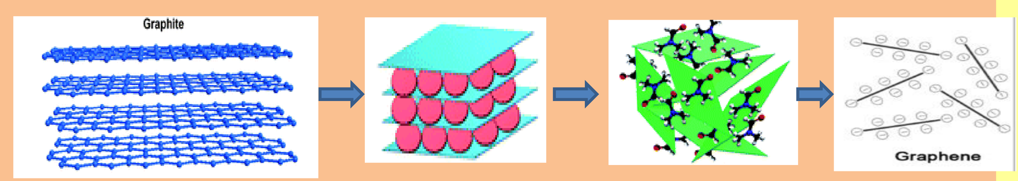


Fig.1. Schematic diagram showing the intercalation and expansion of as received flake graphite

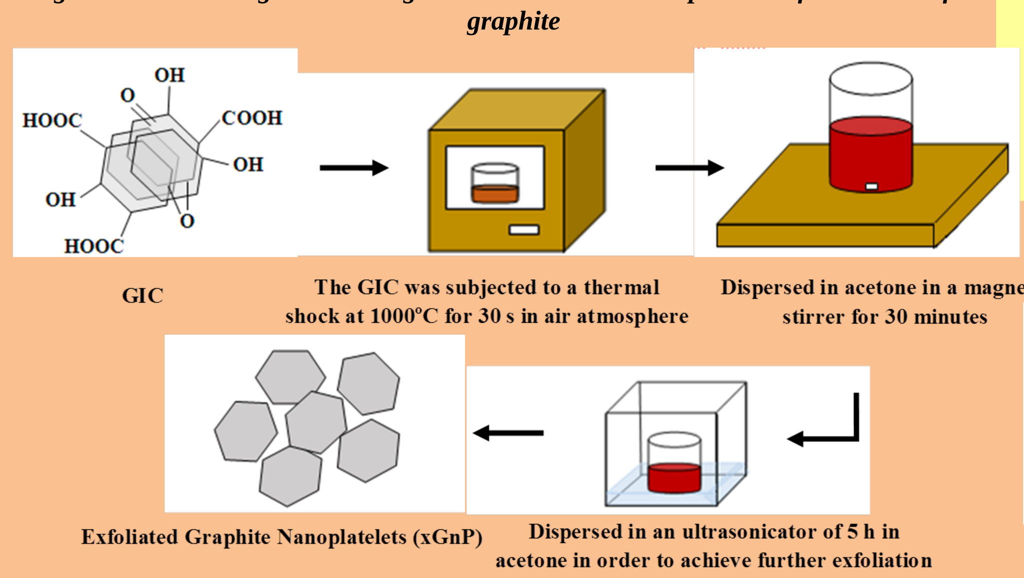


Fig. 2. Schematic diagram illustrating the various steps for the synthesis of xGnP

Synthesis of 1D Carbon Nanotubes

Hydrocarbon gases (Ethylene, Methane, Acetylene ,etc.) + **Process gases** (Ammonia, Nitrogen and Hydrogen)
↓
Pre-treatment and etching of the Fe film to further reduce the size of Fe particle at 10^{-3} vacuum for 20 minutes.
↓
Chemical reaction of the gases ($NH_3/C_2H_2/H_2$) in the ratio of 20:50:20 in a reaction chamber at a temperature of 800°C and 10-3 millibar pressure for 20 minutes on heated metal substrate.
(NH_3 + H_2 for first 10 minutes and C_2H_2 for next 10 minutes)
↓
CNT formation and growth as a result of decomposition of hydrocarbon gases on metal catalyst.

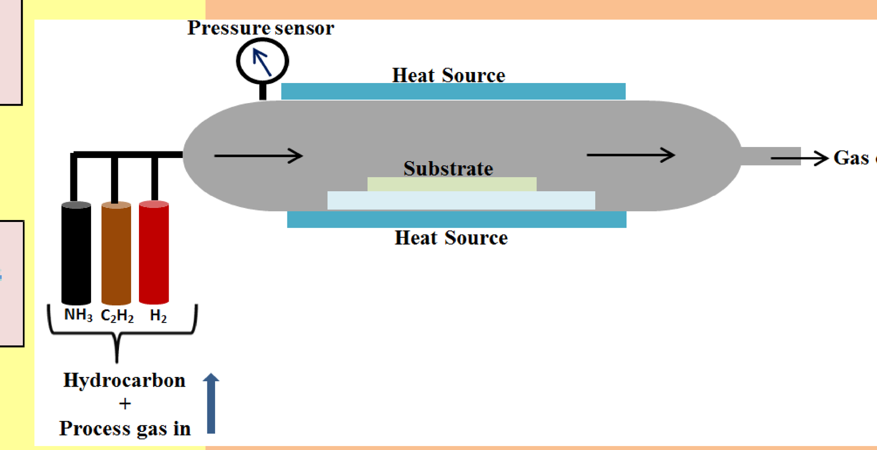


Fig. 3. Schematic illustrating the synthesis of CNTs

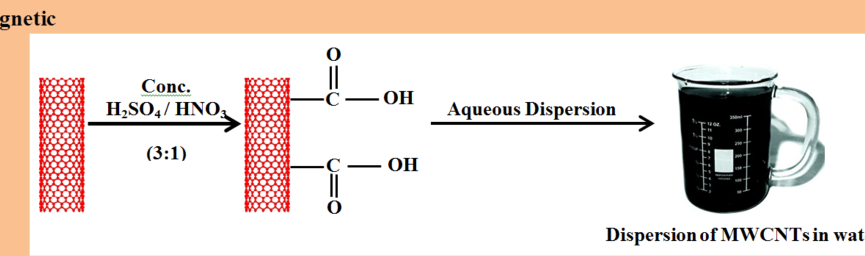


Fig. 4. Functionalisation of CNTs for utilisation as nanoreinforcement in Composite Development

Properties	Graphene	MWCNTs
Tensile strength	125 GPa	60 Gpa
Young's modulus	1.3 TPa	0.3-1 TPa
Thermal Conductivity	~ 5300 W. m^{-1}. K^{-1}	~ 3500 W. m^{-1}. K^{-1}
Electrical Conductivity	~ 15000 cm^2 .V^{-1}.s^{-1}	~ 12000 cm^2 .V^{-1}.s^{-1}
Film Density	~2.26 g/cc	~2.6 g/cc
Surface Area	~ 2630 m^2 /g	~ 600 m^2 /g

Characterisation

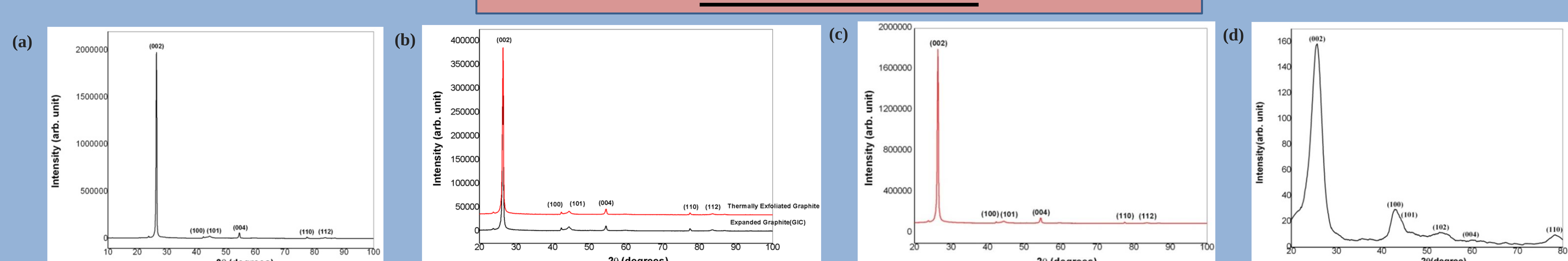


Fig. 5. XRD pattern of (a) NFG, (b) Thermally exfoliated graphite, (c) xGnP, (d) MWCNTs

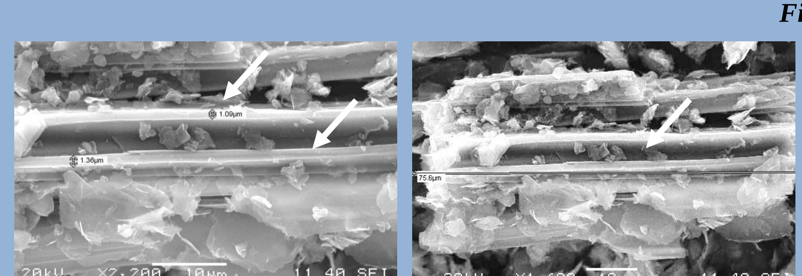


Fig. 6. SEM image of Thermally exfoliated Graphite

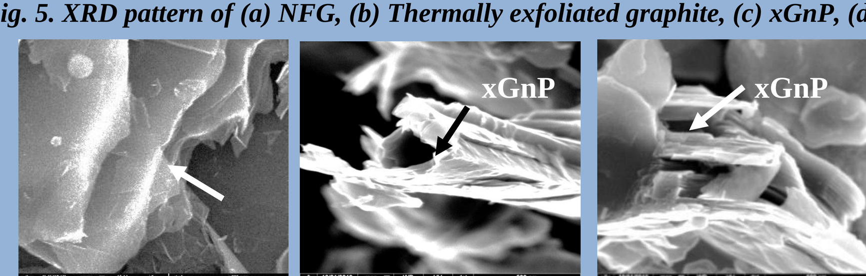


Fig.7. SEM of xGnP

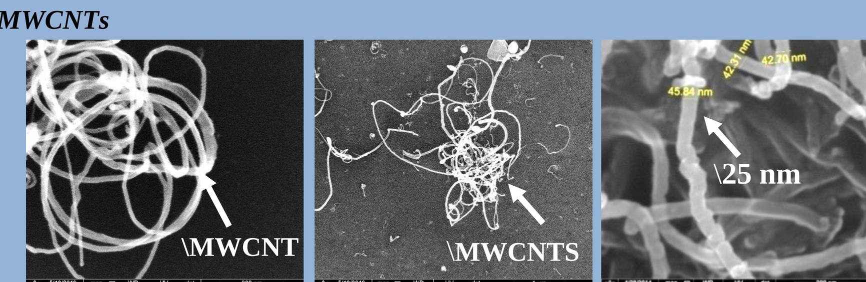


Fig.8. SEM of MWCNTs

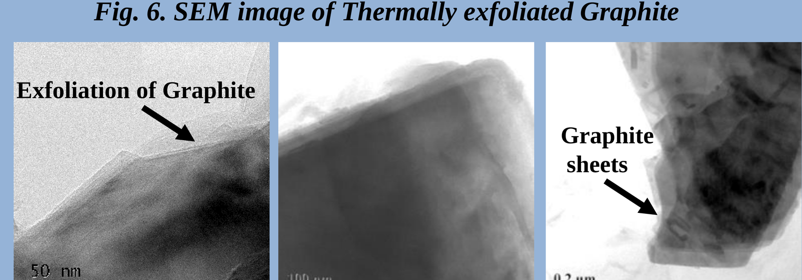


Fig. 9. HRTEM images of Thermally exfoliated Graphite

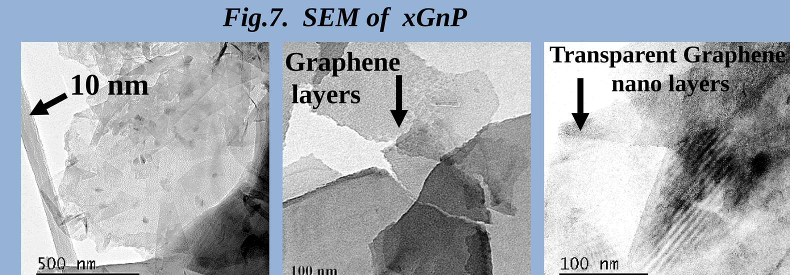


Fig.10. HRTEM of xGnP

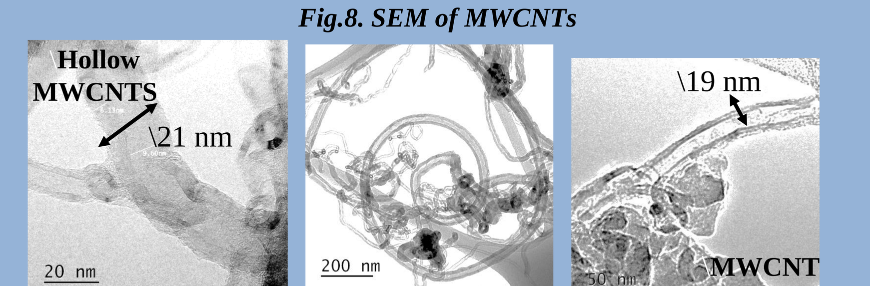


Fig.11. HRTEM of MWCNT

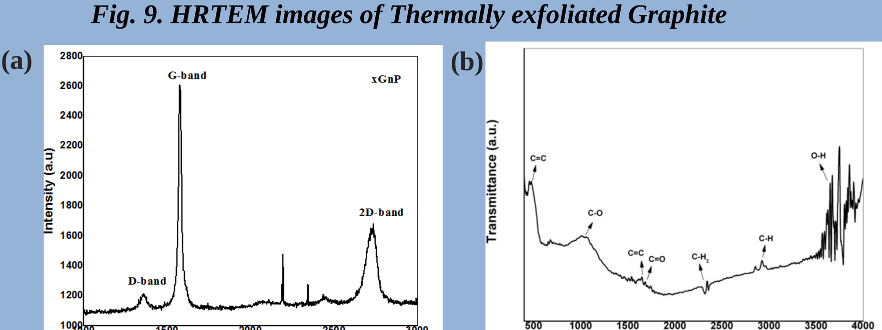


Fig. 12. (a) Raman spectra, (b) FTIR

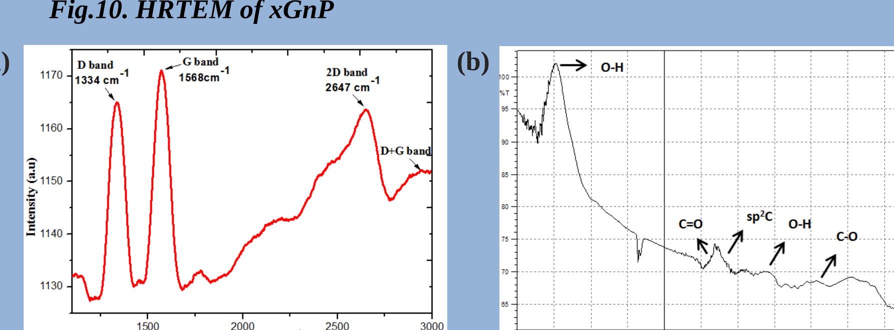


Fig. 13. (a) Raman spectra, (b) FTIR

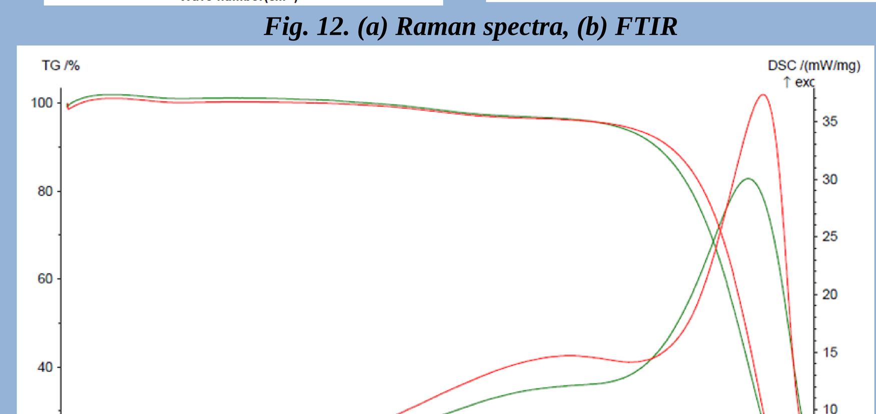


Fig.14. DSC /GA analysis of xGnP

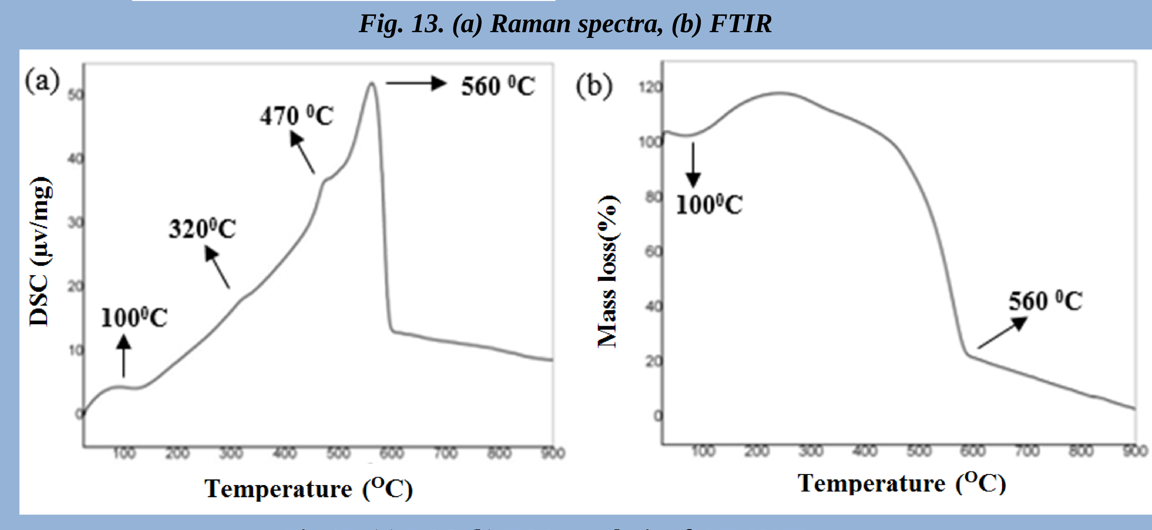


Fig.15. (a) DSC (b) TGA analysis of MWCNTs

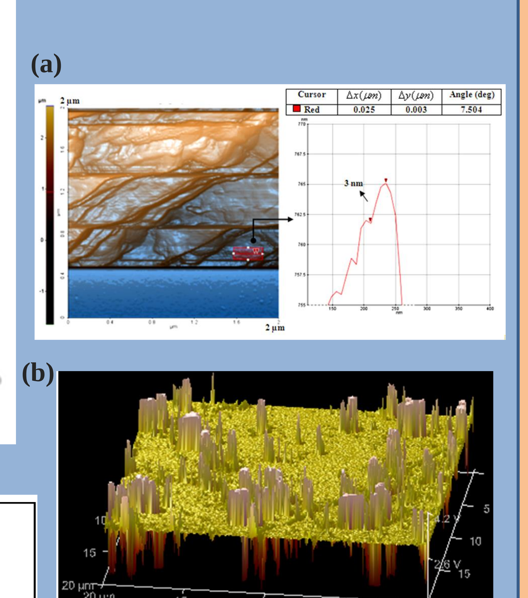


Fig.18. AFM of (a) xGnP, (B) MWCNTs

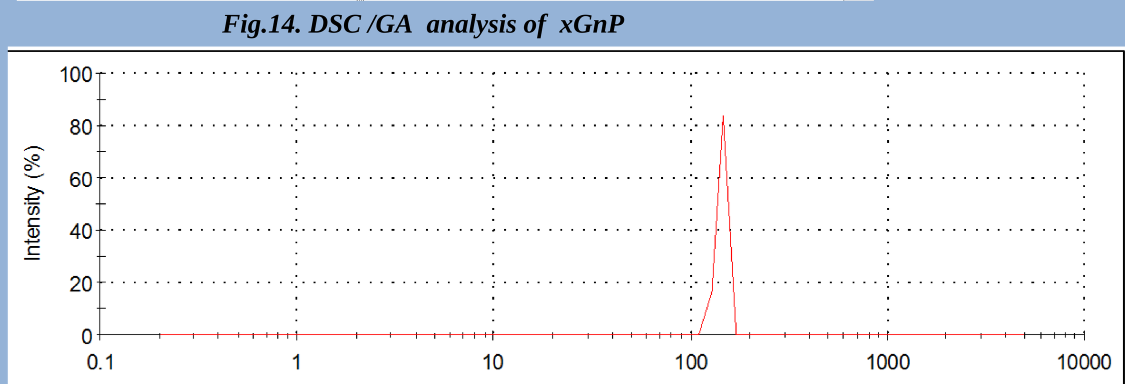


Fig.16. Particle size analysis of xGnP

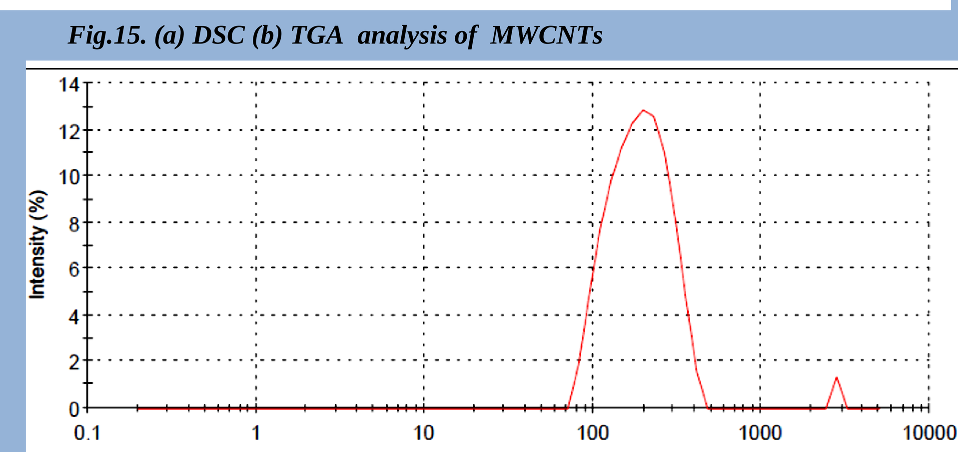


Fig.17. Particle size analysis of MWCNTs

Development of Nanocomposites

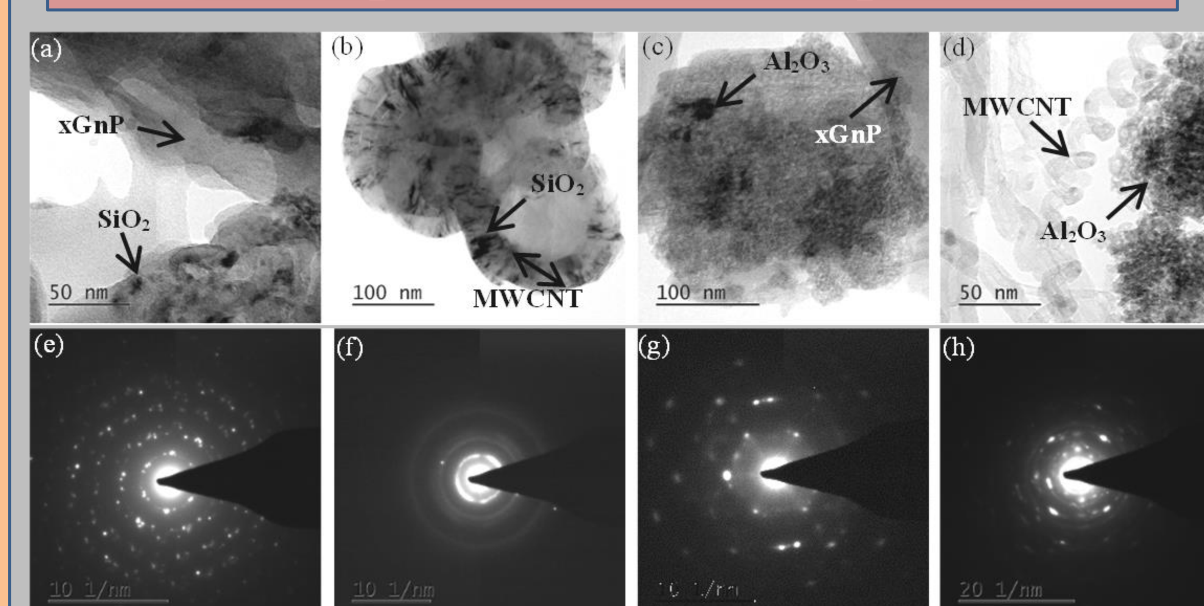


Fig. 19. HRTEM images of (a) SiO_2-3vol.% xGnP; (b) SiO_2-3vol.% MWCNT; (c) Al_2O_3-3vol.% xGnP; (d) Al_2O_3-3vol.% MWCNT and SAD patterns of (e) SiO_2-3vol.% xGnP; (f) SiO_2-3vol.% MWCNT; (g) Al_2O_3-3vol.% xGnP; (h) Al_2O_3-3vol.% MWCNT powder mixtures

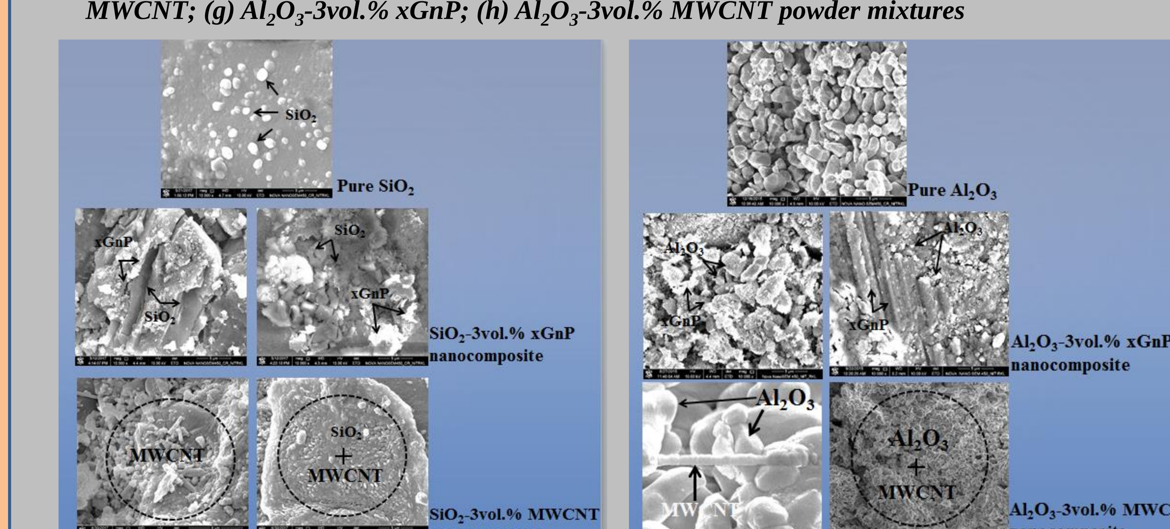


Fig. 20. Development of SiO_2 /Al_2O_3 - xGnP/ MWCNT nanocomposites

SiO_2 /Al_2O_3- xGnP composites SiO_2 /Al_2O_3-MWCNT composites

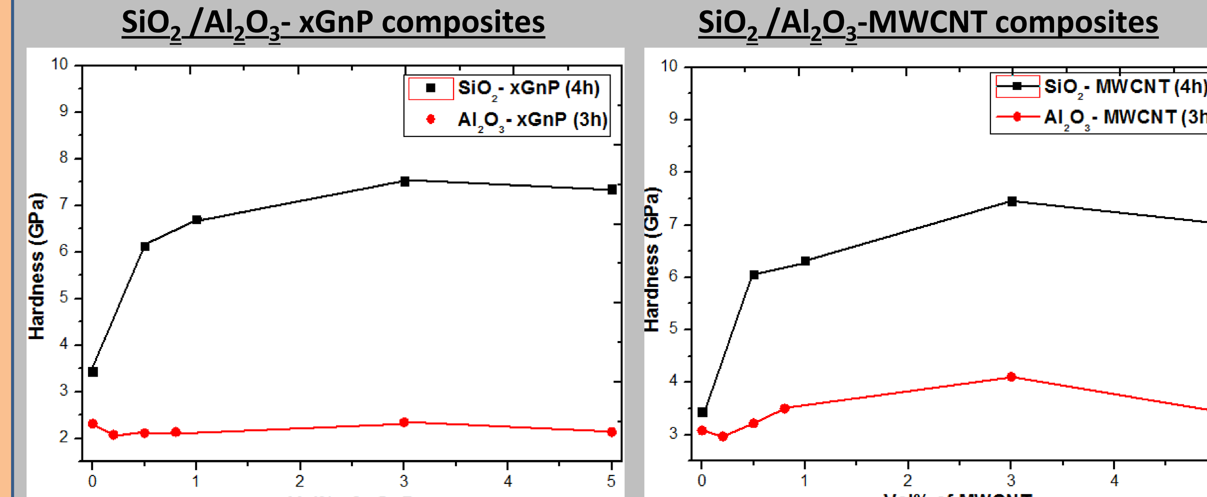


Fig. 21. Variation in Hardness

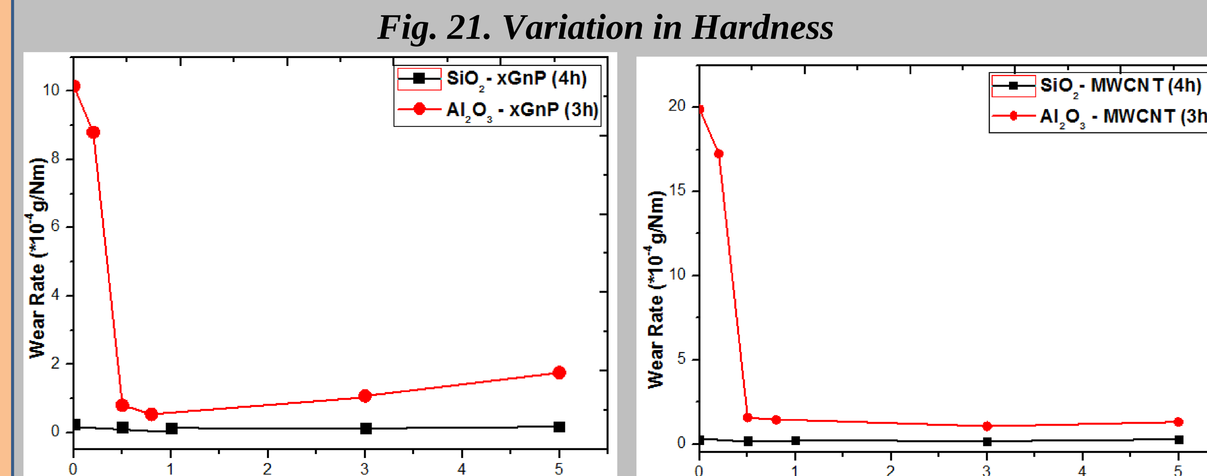


Fig. 22. Variation in Wear Rate

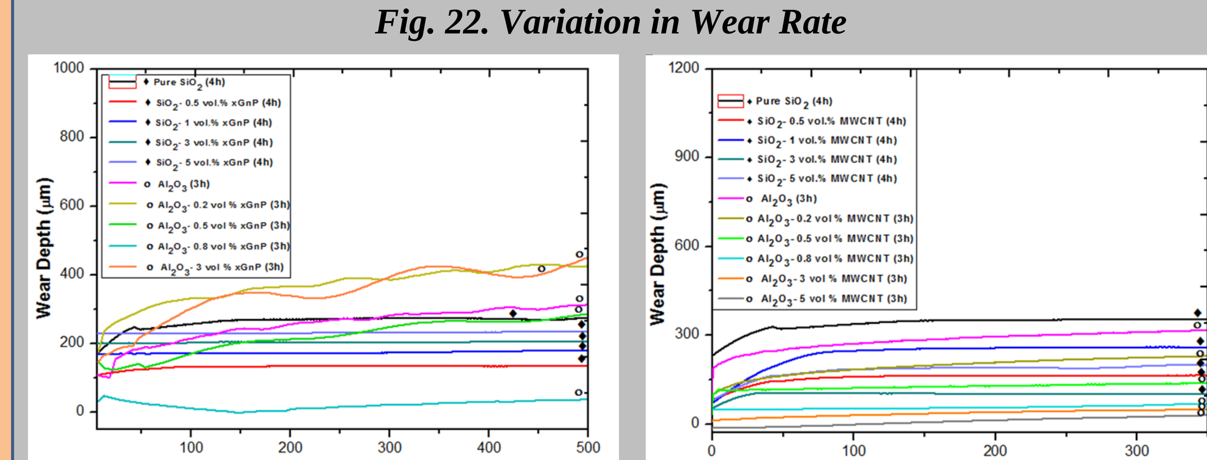


Fig. 23. Variation in Wear Depth

Conclusions

1. Graphene is a novel substitute for CNTs and could serves as a better nanofiller for the development of nanocomposites.
2. Acid Intercalation can serve as easiest medium to produce bulk graphene with least defects.
3. LPCVD process eases the formation of defect free CNTs.
4. Matrix type, shape, size, volume and distribution of nanofillers, filler hardness are the factors that affect the mechanical behaviour of the nanocomposite.
5. Nanofillers like xGnP and MWCNTs are found to be very effective in improving the properties of the composites when added at a lower loading level of upto 3 vol. %.
6. SiO_2-xGnP/MWCNT composites were found to have better mechanical properties as compared to Al_2O_3-xGnP/MWCNT composites.

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References

1. K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V Grigorieva, A. A. Firsov, Science 306 (2004) 666-669.
2. A. K. Geim and K. S. Novoselov, Nature Materials 6 (2007) 183-191.
3. S. Iijima, T. Ichihashi, Single-shell carbon nanotubes of 1-nm diameter Nature 363 (1993), pp. 603-605.
4. T. Kusunose, T. Sekino, Y.H. Choa, K. Niihara, J. Am. Ceram. Soc. 85(11) (2002) 2689–95.
5. H. Conrad, J. Narayan, Scripta. Mater. 42 (11) (2000) 1025–30.