Title: Effect of Sonication on the Exfoliation of Graphite Nanoplatelets

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Abstract

Since its discovery in 2004 graphene has generated huge interest in both academic institutions and industries due to its unrivalled physical properties. Graphene a 2-dimensional material is a one-atom-thick sheet of sp2-bonded carbon and has exceptionally good properties. Apart from the very high modulus of elasticity of ∼1 TPa and tensile strength of ∼125 GPa graphene also has a thermal conductivity of ~3080-5300 W/mK which is 25 times that of Si. It has a carrier mobility at room temperature of 10,000 cm2/VS and a theoretical specific surface area is 2630 m2/g. Large scale economical production of high-quality graphene having few layers is essential for their real-world applications. Here, we report an effective and facile technique for the large-scale production of exfoliated graphite nanoplatelets. The processing route that has been adopted here for the synthesis of graphite nanoplatelets is based on the intercalation of the natural flake graphite (NFG) and solvent dispersion. Microcrystalline natural flake graphite is subjected to intercalation using concentrated sulfuric acid (H_2SO_4) along with hydrogen peroxide (H_2O_2) leading to the formation of a graphite intercalation compound (GIC). The GIC is later thermally exfoliated to obtain the graphite nanoplatelets. The graphite nanoplatelets are finally ultrasonicated in acetone for five different time periods to find the effect of vibrational mechanism on the exfoliation of the graphite nanoplatelets. Ultrasonication has been carried out at room temperature for 2, 5, 7, 12 and 20 h. Both HRTEM and AFM analysis confirm that the nanoplatelets obtained after ultrasonication for more than 12 h were well exfoliated and had a thickness less than 1 nm. The XPS analysis of various samples showed a maximum relative % of C (97.2 at. %) and a minimum relative % of O (2.8 at. %) in the case of 12 h sonicated sample. The surface area and pore size distribution were determined by the Brunauer-Emmet-Teller (BET) method. The extent of defects introduced in the nanoplatelets during ultrasonication was determined from the ID/IG intensity ratio using the Raman spectra obtained from the various ultrasonicated samples. Ultrasonication of the graphite nanoplatelets beyond 5 h shows a gradual increase in crystallinity and decrease in defect density as well as a decrease in the number of graphene layers in the graphite nanoplatelets. Beyond 12 h of ultrasonication both the intensity of the (002) X-ray diffraction peak and the ID/IG ratio of the Raman spectra come to a saturation suggesting that there is a limit to the extent of exfoliation possible by the ultrasonication process. Highly crystalline graphite nanoplatelets having low defect density and consisting of few layers of graphene could be synthesized by ultrasonication of the thermally exfoliated graphite. The process of thermal exfoliation followed by ultrasonication is very effective in producing few layer graphene (FLG) platelets in large quantities.

Keywords: Graphite Nanoplatelets, Graphite Intercalation Compound (GIC), Raman Spectroscopy, HRTEM, AFM

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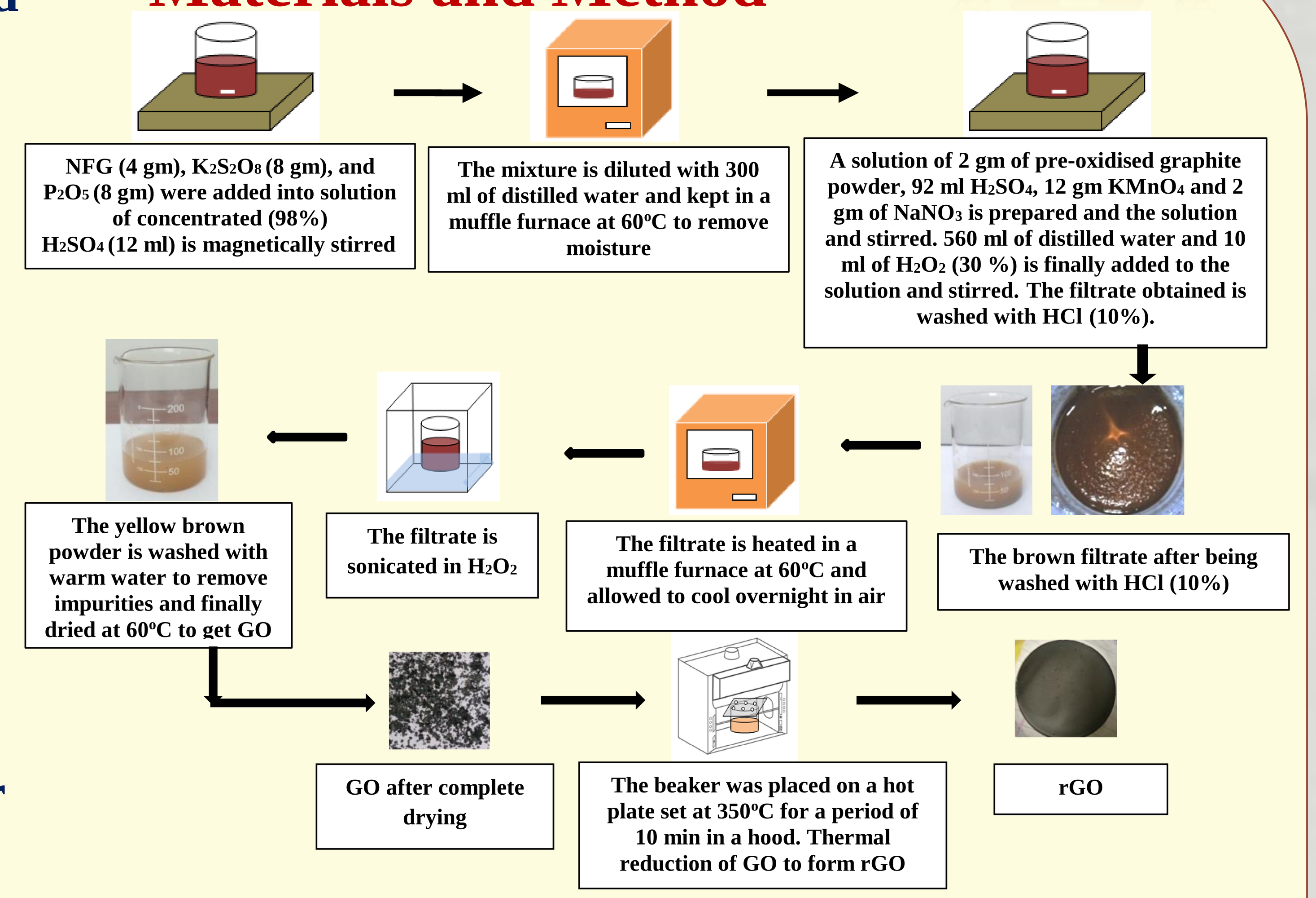
Introduction and Objectives

- Development of graphite nanoplatelets by the solvent dispersion and intercalation of natural flake graphite (NFG).
- The process of thermal exfoliation followed by ultrasonication is capable of producing few layer graphene platelets in large quantities and is an effective and facile technique for the large-scale production of few layer graphene sheets .
- Mass production of high quality graphene materials at low cost for real applications.
- Initially graphite nanoplatelets have been synthesized by thermal exfoliation of the GIC followed by sonication. Highly crystalline natural flake graphite is subjected to intercalation using H_2SO_4 along with H_2O_2 followed by thermal exfoliation which was followed by ultrasonicating the product in acetone for five different time periods to find out the effect of vibrational mechanism on further exfoliation of the thermally exfoliated graphite.
- Ultrasonication has been carried out at room temperature for a period of 2, 5, 7, 12 and 20 h.
- The effect of sonication on the extent of exfoliation of the thermally exfoliated graphite was analyzed using several analytical techniques like XRD, HRTEM, SEM, SFM, XPS, Raman spectroscopy and FTIR in order to find out the optimum time of sonication which could result in maximum extent of exfoliation in the graphite platelets without imparting defects to it.
- Effort has been made to synthesize graphite nanoplatelets comprising few layered high quality graphene by sonication of the thermally exfoliated graphite.

Materials and Method

Intercalation of As-received Natural Flake Graphite
↓
Solvent Dispersion
↓
Formation Of GIC (Expanded Graphite) (-Gr-H_2SO_4-Gr--H_2SO_4-)
↓
Thermal Exfoliation
↓
Sonication in Acetone For 5, 7, 12, 20 h at Room Temperature
↓
Graphite Nanoplatelets



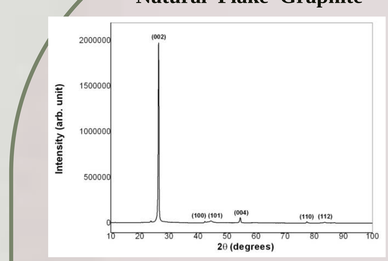
Acetone is used for sonication due to its polar nature. It enables the sonication process to be carried out at higher energies without raising the temperature and without damaging the solute particles

Sonication and Its Relevance

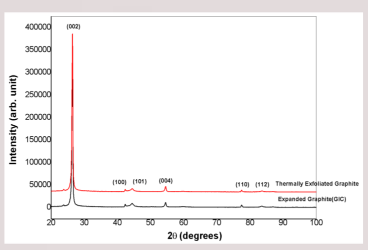
- Sonication is the act of applying sound energy to agitate particles in the sample.
- Usually ultrasonic frequencies are kept > 20 KHz
- It can be used for the production of nanoparticles, for speed dissolution, provide energy for certain chemical reactions, evenly dispersing nanoparticles in liquids, initiate crystallisation process, isolate small crystals or aid in mixing.

Results and Discussions

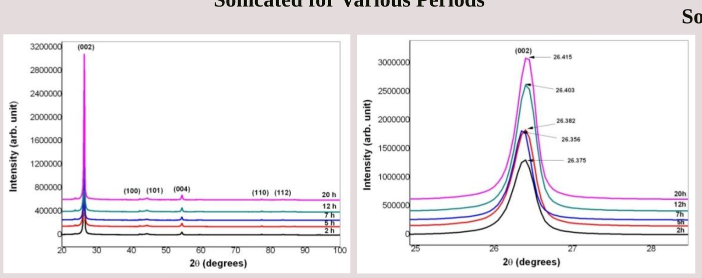
XRD of As-Received Natural Flake Graphite



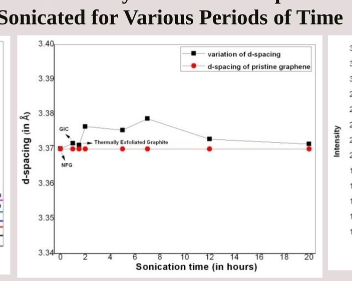
Expanded graphite (GIC) and Thermally Exfoliated graphite



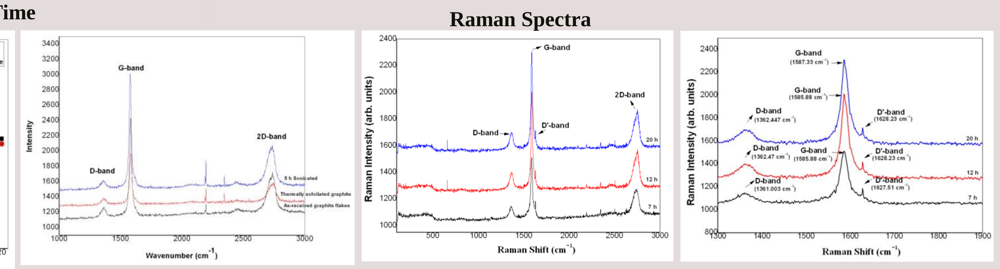
Thermally Exfoliated Graphite Sonicated for Various Periods



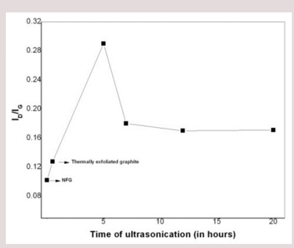
Variation of d-spacing of the GIC, xGNP and Thermally Exfoliated Graphite Samples Sonicated for Various Periods of Time



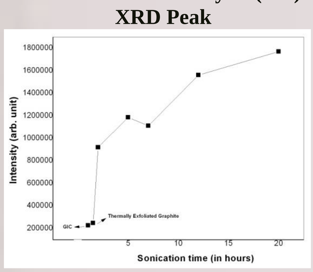
Raman Spectra



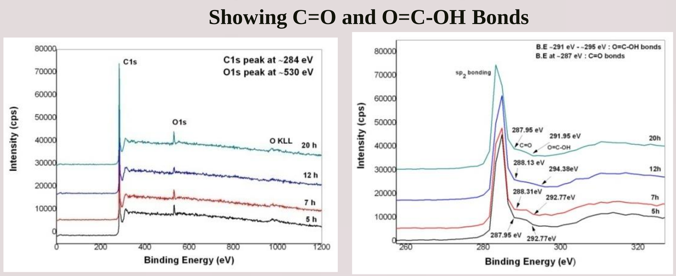
ID/IG Ratio



Variation of Intensity of (002) XRD Peak

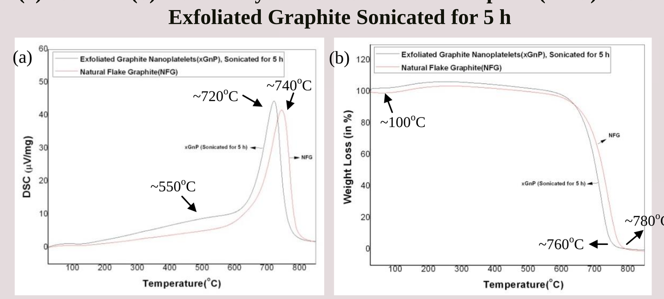


High Resolution C1s XPS Spectra Showing C=O and O=C-OH Bonds

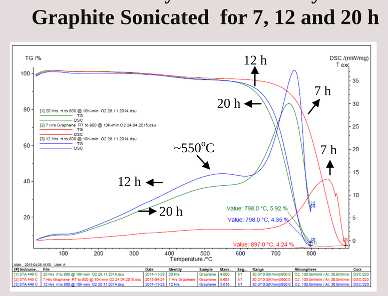


Hours of Sonication	Peak	Peak Binding Energy (eV)	Relative % of C and O in Exfoliated Graphite Nanoplatelets (xGnP)
5 h	C1s	284.906	C- 96.2 atomic % O- 3.8 atomic %
7 h	C1s	284.72	C- 96.2 atomic % O- 3.8 atomic %
12 h	C1s	284.906	C- 97.2 atomic % O- 2.8 atomic %
20 h	C1s	283.29	C- 95.2 atomic % O- 4.8 atomic %

(a)DSC and (b) TGA Analysis of Natural Flake Graphite (NFG) and Exfoliated Graphite Sonicated for 5 h



DSC and TGA Analysis of Thermally Exfoliated Graphite Sonicated for 7, 12 and 20 h



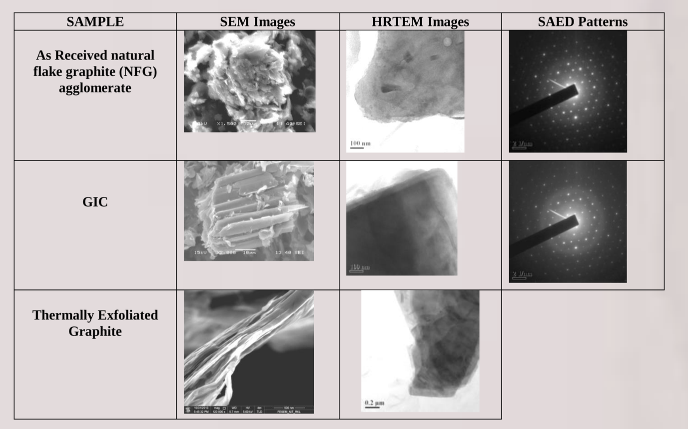
d-spacing , 2θ and Intensity of the (002) XRD peak of NFG , GIC, Thermally Exfoliated Graphite and the Thermally Exfoliated Graphite Samples Sonicated for Various Periods of Time.

Sample	d-spacing (Å)	2θ(degree)	Intensity (arb. units)
Expanded graphite (GIC)	3.3716	26.413	226561
Thermally Exolfiated graphite	3.3711	26.417	247777
Thermally Exolfiated graphite sonicated for 5 h	3.3754	26.382	1185333
Thermally Exolfiated graphite sonicated for 7 h	3.3787	26.356	1111333
Thermally Exolfiated graphite sonicated for 12 h	3.3728	26.403	1561235
Thermally Exolfiated graphite sonicated for 20 h	3.3714	26.415	1769402

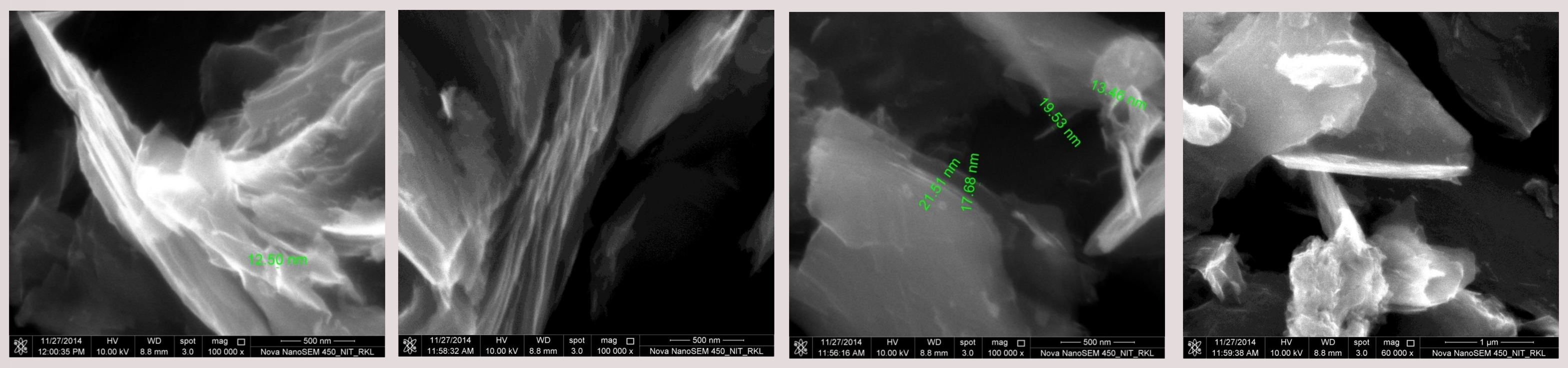
BET Analysis

Hours of Sonication	Area (m^2/g)	Total Pore Volume (cc/g)	Average Pore Diameter (Å)
7	2.221×10^{-1}	7.694×10^{-3}	1.386×10^{3}
12	2.465×10^{-1}	8.565×10^{-3}	1.390×10^{3}
20	3.047×10^{-1}	10.44×10^{-3}	1.371×10^{3}

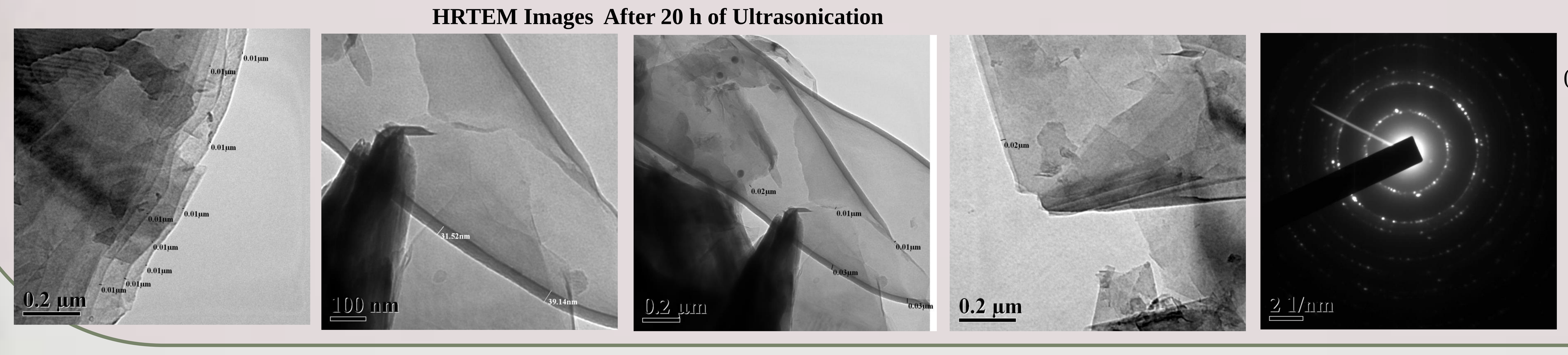
SEM Images of NFG, GIC and Thermally Exfoliated Graphite



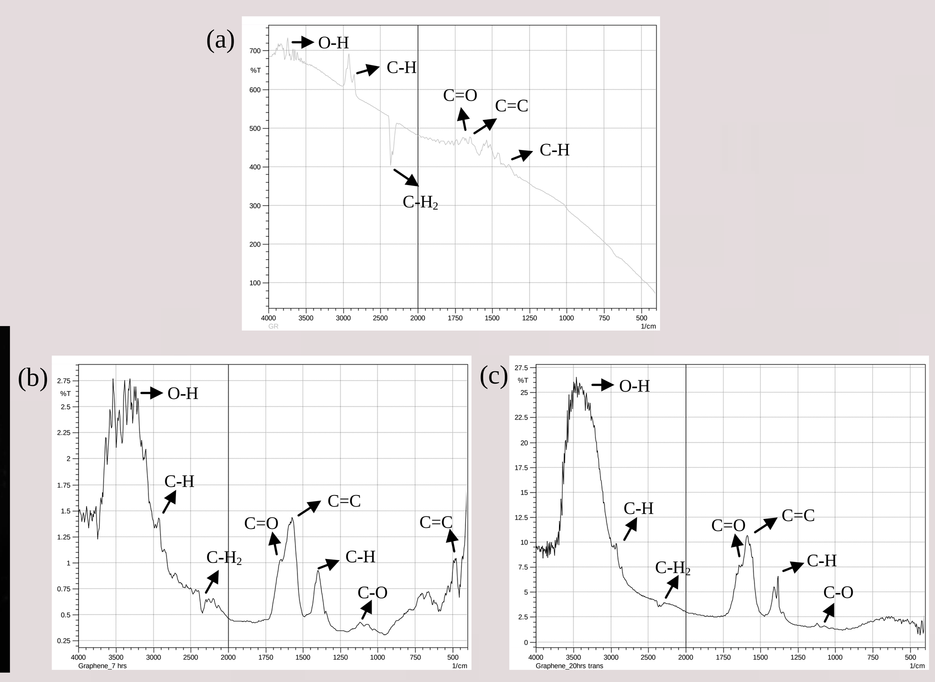
SEM Images After 20 h of Ultrasonication



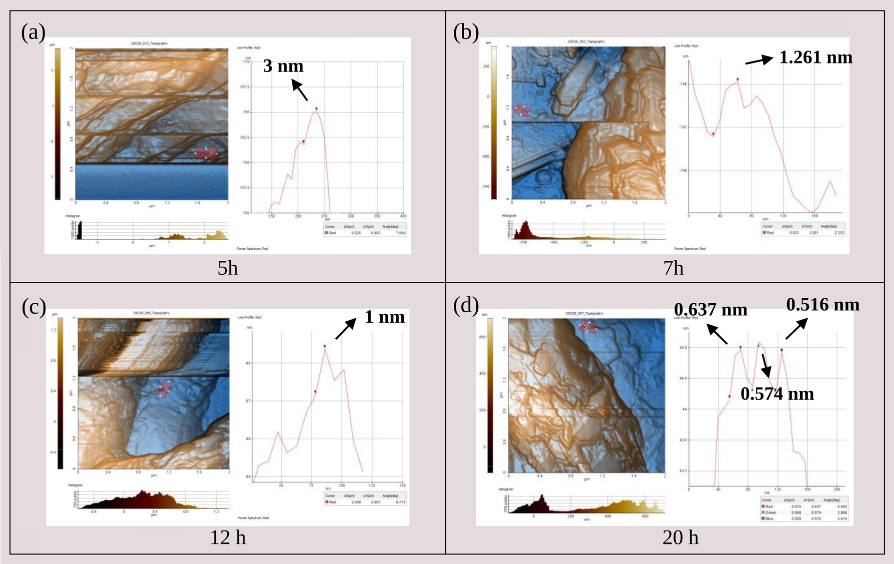
HRTEM Images After 20 h of Ultrasonication



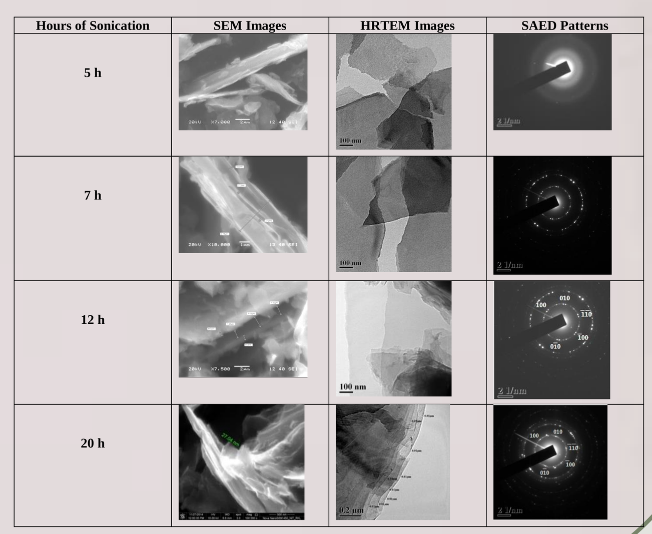
FTIR of (a) NFG (b, c) Thermally Exfoliated Graphite Ultrasonicated for 7 and 20 h



High Resolution Tapping Mode AFM Image of the Graphite Nanoplatelets Developed by Sonication of the Thermally Exfoliated Graphite for Various Periods of Time Deposited on a Mica Substrate



HRTEM of Ultrasonicated Samples of Thermally Exfoliated Graphite



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Conclusions

- Highly crystalline graphite nanoplatelets having low defect density and consisting of few layers of graphene could be synthesized by sonication of the thermally exfoliated graphite.
- Sonication of the thermally exfoliated graphite beyond 5 h shows gradual increase in crystallinity and decrease in defect density along with the increase in the number of graphene layers in the graphite nanoplatelets.
- Beyond 12 h of sonication both the intensity of the (002) XRD peak and the ID/IG ratio of the Raman spectra come to a saturation suggesting that there is a limit to the extent of exfoliation possible by the sonication process.
- The results of both the HRTEM and AFM analysis suggest that the graphite nanoplatelet samples sonicated beyond 12 h are well-exfoliated and have a thickness less than 1 nm.
- The DSC results suggest that the thermal degradation of the graphite nanoplatelet samples that have been sonicated for a longer period of time starts prior to the degradation of the graphite nanoplatelet samples that have been sonicated for a shorter period of time. The thermal degradation of the graphite nanoplatelets start at around 620^{o}C and by 800^{o}C the degradation of the graphite nanoplatelets is complete.