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**Electrochemical synthesis and characterization of few layer graphene
nanosheets**

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Abstract

Electrochemical synthesis of few layered graphene nanosheets (FLGNSs) by intercalation and exfoliation of pyrolytic graphite sheet in a simple protic, H₂SO₄ electrolyte has been investigated in the present report. The as-prepared FLGNSs were characterised by X-ray diffraction, Field emission scanning electron microscopy, Raman spectroscopy, Fourier transform infrared spectroscopy, UV-visible spectroscopy and Atomic force microscopy. From the analyses, surface oxygenation, defect-rich FLGNSs has been confirmed.

1. Introduction

Graphene nanosheets (GNSs) are considered to be the two-dimensional basis of other allotropes of carbon possessing many extraordinary properties, such as high mobility of charge carriers, high mechanical strength, extremely high thermal conductivity as well as interesting optical characteristics [1-3]. Different techniques have been reported to obtain GNSs such as, micromechanical exfoliation [4], chemical oxidation of graphite powder followed by its reduction [5], epitaxial growth in ultra-high vacuum process [6] and chemical vapor deposition [7] process.

Despite of many available techniques, electrochemical exfoliation route of production of GNSs are simple, economic, non-destructive, environmentally friend, operates at ambient temperature

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and pressure and provide thickness control by adjusting the bias potential applied to the electrodes.

2. Experimental

2.1. Materials

Pyrolytic graphite sheet of thickness 3 mm (Asbury Graphite Mills, AR-12) were employed as both the electrodes in an electrochemical cell. 1.0 M of H₂SO₄ was taken as electrolyte for the synthesis of FLGNSs.

2.2. Preparation of FLGNSs colloid solution

The electrochemical exfoliation process was carried out by applying DC bias on the graphite electrode from 0 to +10 V in ramp wise. The graphite anode of 20 mm × 20 mm × 3 mm is exposed in 1.0 M H₂SO₄ electrolyte. After exfoliation of graphite sheets, the suspensions were filtered from electrolyte and wash in DI thoroughly. It is then subjected to bath sonication for 30 minutes for well dispersion in DI water.

2.3 Characterisation

As-prepared FLGNSs colloid and pyrolytic graphite sheets were subjected to various structural, morphological, topographical, chemical bonding and functional group analyses by high precision and calibrated scientific instruments. The analysing instruments like X-ray diffraction (XRD), Field emission scanning electron microscope (FESEM), Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR), UV-visible spectroscopy and Atomic force microscopy (AFM) has been used.

3. Results and Discussion

In this experiment, we performed electrochemical intercalation and exfoliation of pyrolytic graphite sheets in 1.0M H₂SO₄ electrolyte. The static bias of +1 V is applied to the graphite electrodes for 5 minutes, followed by two step of ramping the bias to +5 V for 2 minutes to finally at +10 V. The initial low potential is given for wetting the electrode and physical adsorption of SO₄²⁻ ions to the grain boundary of graphite. Initially at low ramp bias the exposed part of graphite in the electrolyte has been expanded by gaseous species released from intercalate

of sulphate ion. Once high bias (+ 10 V) was applied, the graphite was quickly dissociated into small pieces and spread in the electrolyte.

3.1. XRD analysis

Fig. 1 show the XRD patterns of the pyrolytic graphite sheet and electrochemical exfoliated FLGNSs at 1.0 M H₂SO₄ electrolytes. The four intensive peaks at 26.39°, 42.38°, 44.33°, and 54.29° (2θ values) corresponding to 002, 100, 101, and 004 crystal planes of the graphite sheet, respectively (ICCD-PDF # 411487) shown in Fig. 1a. After electrochemical exfoliation, the 002 basal plane of the graphite sheets has been expanded and formed as FLGNSs as confirmed from the peak broadening and shifting towards the lower angle to 23.21° as shown in Fig. 1b. However, due to anodic oxidation reaction, there might possibilities of partial oxygenation of the FLGNSs as observed form the XRD peak at 11.75°, which corresponding to 001 plane of graphene oxide (GO) nanosheets.

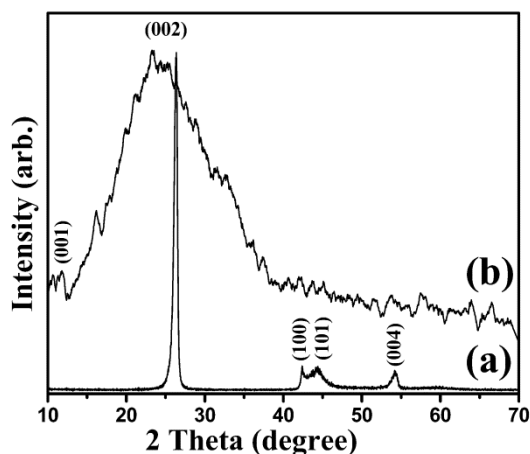


Fig. 1: XRD patterns of graphite sheet (a) and exfoliated FLGNSs (b).

3.2. FESEM analysis

Fig. 2a shows the cross-sectional FESEM morphology of the layered structure of graphite sheet used before electrochemical exfoliation process. The image reveals the highly oriented stratified graphitic planar sheets. After intercalation of sulphate ions, the van der Waal's force of bonding in between the graphite plane has been reduced and exfoliated as FLGNSs as shown in Fig. 2b. The crumpling edge of FLGNSs has also been observed, due to enrichment of oxygen functional group covering around it.

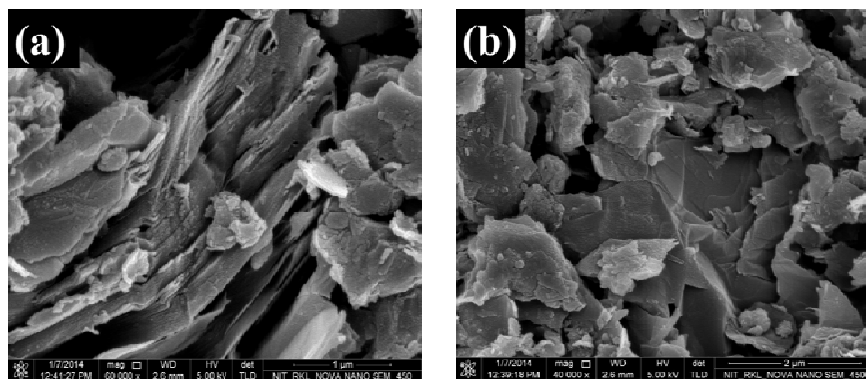


Fig. 2: FESEM image of (a) Pyrolytic graphite cross-section and (b) electrochemical exfoliated FLGNSs.

3.3. Raman spectroscopy analysis

Raman spectroscopy is a fast, non-destructive and unique informative technique used to study structures and defects of sp^2 hybridized carbon and its allotropes. The characteristic bands for pyrolytic graphite and FLGNSs were observed around 1354 and 1590 cm^{-1} corresponding to D and G bands respectively as shown in Fig. 3. The D band is due to the presence of defects or disorders in sp^2 structure, particularly at the edges of graphene sheets arising from a breathing mode of k-point phonons of A_{1g} symmetry. The G band is a signature of true hexagonal carbon rings that arise from in-plane C-C bond-stretching motions, physically corresponding to first-order scattering of the E_{2g} phonon at the Brillouin zone centre. The broader and strong D band, having full width at half maximum of 88 cm^{-1} , (Fig. 3b) show more disorderness compared to the graphite (Fig. 3a) at the edges which should be due to the linear increase of oxidation during intercalation and exfoliation. Moreover defect density in the carbon sp^2 structure can be quantified by I_D/I_G ratio and was found to be around 0.39, and 0.98 for graphite sheet, and 1.0 M H_2SO_4 for exfoliated FLGNSs respectively.

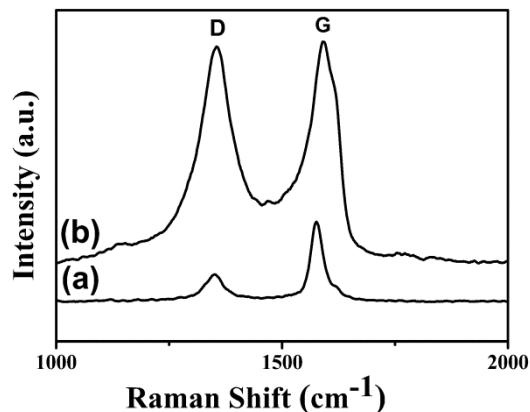


Fig. 3 - Raman spectrum of Pyrolytic graphite (a) and electrochemical exfoliation of FLGNSs (b).

3.4. FTIR analysis

FT-IR spectra of pyrolytic graphite sheets (Fig. 5a.) and exfoliated FLGNSs (Fig. 5b.) has been analysed. Due to anodic oxidation reactions, various oxygen functional groups have been attached on exfoliated FLGNSs. An intense and broad peak around 3500 cm^{-1} is observed in FLGNSs spectra due to stretching vibrations of O-H functional group. Two consecutive peaks at 2927 and 2862 cm^{-1} in spectrum confirms C-H stretching and the C-H bending band at 1445 cm^{-1} shows hydroxylation of graphene sheets³³. The characteristics infrared (IR) absorbance at 1668 cm^{-1} , is the evidence for C=C bond stretching in aromatic ring of carbon sheet respectively^{60,61}. Edge and surface oxygen/hydrogen endowment on the exfoliated graphene sheets can also be visible from different IR absorbance peaks including 1096 (C-O stretching; alkoxide), 1255 (C-O-C stretching; epoxide), and 1384 cm^{-1} (COO-H/CO-H stretching; carboxyl)^{44,60,61}. The presence of a sharp band at 858 cm^{-1} in Fig. 5b, attributed to the aromatic signal of exfoliated graphene sheets, and may be due to the severe oxygenation on the hexagonal structural damage the graphene sheets³⁶ in the solutions.

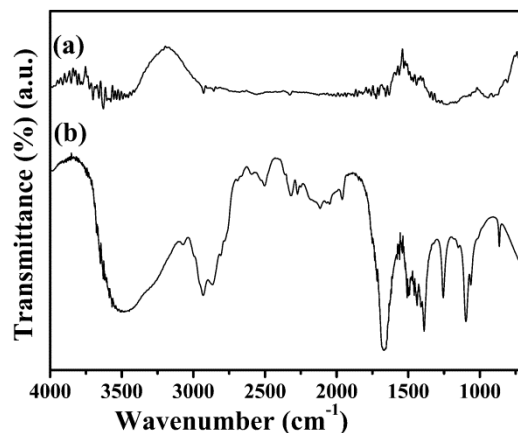


Fig. 5 FTIR spectra of pyrolytic graphite sheets (a) and exfoliated FLGNSs.

3.5. UV-visible spectroscopy analysis

UV-visible absorption spectroscopy was used for further investigation of the quality of the electrochemically exfoliated FLGNS samples. Fig. 6 shows the UV-Visible spectrum of electrochemically exfoliated FLGNSs colloids. The strong absorbance peak at 264 nm impute to π - π^* transitions in aromatic ring of graphene sheets^{46,62}. Further, a broad shoulder around 290 nm in both the exfoliated dispersions is attributed to the n- π^* transitions owing to the presence of C=O bonds⁶⁰ mostly at the edges of thin sheets.

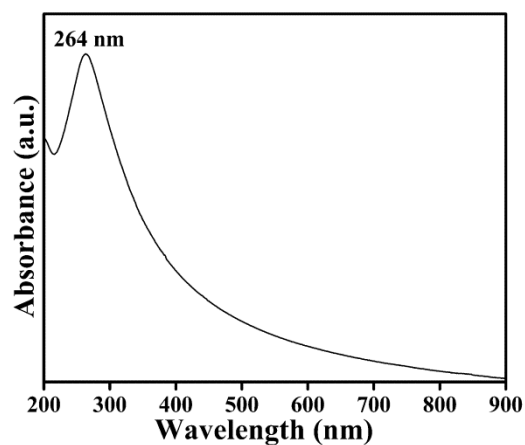


Fig. 6 - UV-vis spectrum of electrochemical exfoliated FLGNSs.

3.6. AFM analysis

The electrochemical exfoliated FLGNSs, coated on silicon wafer were analysed by AFM as shown in Fig. 7 with inset line profile measurement. Graphitic platelets are evenly distributed on silicon substrate. The image reveals the stratified and planer nature of obtained FLGNSs. The line scan shows the average topographic height of these nano sheets is measured to be about 4 to 6 nm indicating 3 to 6 few individual layers of graphene nano sheets [36,46].

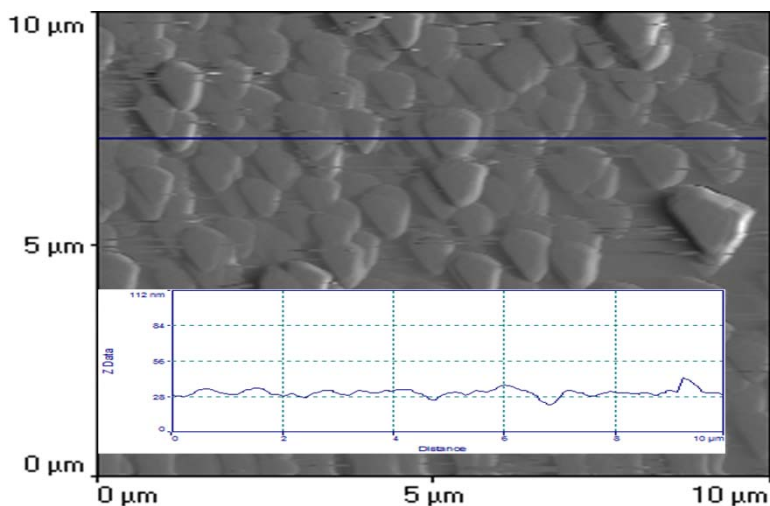


Fig. 4 AFM image of electrochemical exfoliated FLGNSs.

4. Conclusion

In summary, we have carried out a simple and fast electrochemical intercalation and exfoliation process for the production of FLGNSs at industrial scale. From various analyses, it has been observed that the electrochemical exfoliation process though produce various oxygenated functionalization and defect rich graphene nano sheets, can be optimized by selecting suitable types of intercalates and applied bias.

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