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Electrochemical exfoliation of graphite for producing graphene using saccharin

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A green electrochemical exfoliation route to produce graphene from graphite electrode has been provided. Saccharin which is a non-toxic and biocompatible artificial sweetener was used as an intercalating agent in aqueous media. Graphene samples were produced using five different exfoliation potentials. Microscopic and spectroscopic analysis confirmed the presence of few layer graphene sheets in as-exfoliated product. Important observations made were: (a) graphene layers from nano-to-micro meter sizes were produced; (b) number of graphene layers decreased with increase in the intercalation potential, (c) yield of graphene increased with increase in the exfoliation potential and (d) defect density in the exfoliated graphene layer was sensitive to the exfoliation potential in a way that with increase in the exfoliation potential the defect density initially increased and then eventually decreased.

Introduction

Graphene is a two dimensional single layer material made up of sp^2 hybridized carbon atoms.[1,2] Graphene exhibits excellent electrical and thermal conductivity, optical and mechanical properties and phenomenon such as quantum hall effect.[3] These properties have made graphene a versatile material with potential applications in solar cells,[4] composite materials,[5] fuel cells,[6] gas sensors[7] to name a few. The increasing interest in graphene has led to the development of various methodologies for producing high quality graphene in bulk quantities. After its inception form scotch tape assisted exfoliation of graphite by Novoselov *et al.*,[8] graphene is now synthesized routinely in large quantities using techniques such as, chemical synthesis,[9] hydrothermal reduction,[10] chemical vapor deposition,[11] electrochemical exfoliation[12] *etc.* Among these methods, electrochemical exfoliation method has attracted special interest due to its low cost, eco-friendly and non-equipment intensive nature as compared to the other processes.

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Generally, acids, bases, ionic liquids and surfactants are used as electroactive media for synthesizing graphene by the electrochemical exfoliation process. Mahanandia *et al.*[13] have demonstrated an electrochemical technique that utilizes oxalic acid as the electrolyte for high yield of layered graphene sheets directly from graphite.[13] Liu *et al.*[14] exfoliated graphite by anodic electrochemical process using protonic acids like H_2SO_4, H_3PO_4 and $H_2C_2O_4$ in the voltage range of 6–8 V. Among all the protonic acids, H_2SO_4 is most popularly used to exfoliate graphite or generally weaken the bond between graphitic layers because of relatively large ionic size of SO_4^{2-} ion (0.46 nm) compared to the interlayer spacing (0.335 nm) between graphitic layers.[14] Zhou *et al.*[15] cathodically exfoliated graphite using $(Na^+(DMSO)_yC_n^-)$ complex ion. The ionic size of $(Na^+(DMSO)_yC_n^-)$ cation is 1.246 nm, which is almost four times larger than the natural graphite interlayer spacing (0.335 nm).[15] Hence, intercalation of this large cation into cathodic graphite induces huge internal stress within the graphitic layers leading to exfoliation.[15] These reports illustrate that the synthesis of graphene from electrochemical exfoliation of graphite is possible by both anodic and cathodic exfoliation processes.

Ionic liquids, inorganic acids and bases that are generally used as electroactive media for electrochemical exfoliation of graphite[14,15] are highly corrosive and toxic in nature. Hence there exists a need for identifying green, non-toxic compounds that can be used for large scale exfoliation process.[16] In the present work, saccharin which is an edible, green and non-toxic[17] organic compound has been used as intercalating molecule for the exfoliation of graphite[17] to produce graphene. Graphite rod was exfoliated at different intercalation potential and the as-synthesized graphene samples were characterized.

Experiment

Chronoamperometry technique using CHI electrochemical workstation (US make) was employed for electrochemical exfoliation of graphite. Three electrode system with two graphite rods (Alfa Aesar, INDIA) and platinum foil were used as cathode,
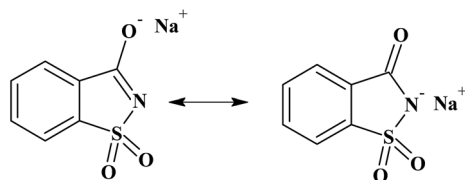
Fig. 1 Resonance structures of sodium saccharin.

anode and quasi-reversible electrodes respectively. Aqueous solution of 0.1 M sodium saccharin solution prepared using millipore water was used as electroactive media. Resonance structure of sodium saccharin is provided in Fig. 1. Exfoliation process was carried out at 2, 4, 6, 8 and 10 V for 10 h. The exfoliation process was carried out in two steps involving initial anodic intercalation of saccharin anion followed by cathodic reduction. For the first 5 h, electrochemical intercalation of

saccharin anion into graphite anode occurred. After 5 h polarity of the electrodes was switched. From the graphite cathode which was anode for first 5 h a stable graphene suspension was obtained. Even during intercalation process in the first 5 h some amount of exfoliated product was observed.

After the exfoliation process, the collected samples were sonicated for 1 h to get aqueous suspension. This graphene suspension was centrifuged at 100 rpm for 10 min to precipitate the heavy particle impurities that got settled at the bottom of the centrifuge tube. The fine suspension in the upper part of the tube was then washed with water and centrifuged again at 8000 rpm for 10 min to isolate the graphene. After washing five times, samples were subjected to characterization process using microscopic and spectroscopic techniques.

X-ray diffraction pattern from graphene samples were obtained using X-pert pro X-ray diffractometer employing a Cu-K_α radiation ($\lambda = 0.1540$ nm) source. Raman spectrum from the exfoliated samples were obtained using microscope setup (HORIBA JOBIN YVON, Lab RAM HR) consisting of diode-pumped solid-state laser operating at 532 nm with a charge coupled detector. UV-visible absorption spectroscopic experiments were carried in 700 to 200 nm wavelength range using Perkin-Elmer (Lambda 35) UV-vis spectrometer. Electron micrographs of graphene samples drop dried on silica substrate were acquired using JOEL-JEM-1200-EX II scanning electron microscope (SEM) operating at 20 kV. A 300 keV field emission FEI Tecnai F-30 transmission electron microscope (TEM) was used for obtaining TEM bright field images of exfoliated graphene samples. Samples for the TEM based analysis were prepared by drop drying graphene dispersion on a carbon coated copper grid. Atomic force microscopy (AFM) experiments were carried at room temperature using Nanosurf AFM instrument (Switzerland). Graphene–water dispersion was drop dried over silica substrate for the AFM based analysis.
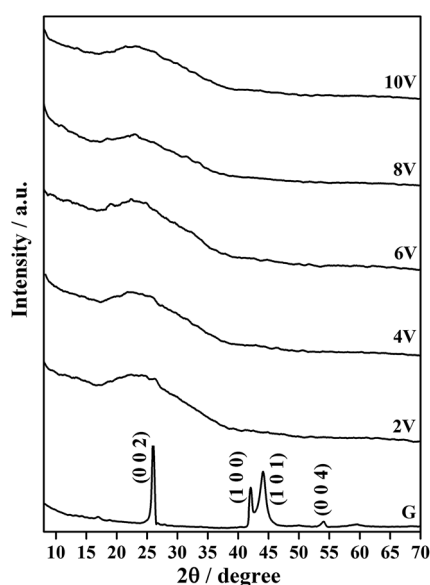
Results and discussion

XRD profiles obtained from all the exfoliated samples and the graphite rod are shown in Fig. 2. The graphite rod exhibited four
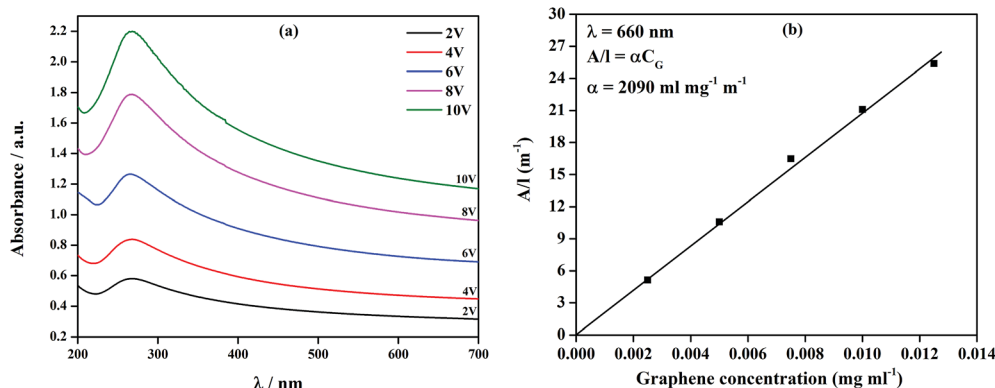

Fig. 2 XRD pattern of graphite and graphene synthesized at different intercalation potential.

Fig. 3 (a) UV-visible absorption spectra of electrochemically exfoliated samples at different potential with saccharin as an intercalating agent and (b) optical absorbance (λ_{660} nm) per unit length (A/l) as a function of concentration of graphene. Insert text shows Lambert–Beer law with an absorption co-efficient $\alpha = 2090$ ml mg^{-1} m^{-1}.
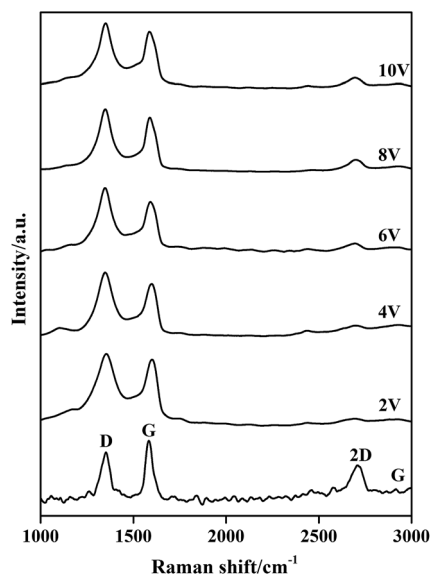
Fig. 4 Raman spectra of graphite and graphene prepared at different potentials.

Table 1 Defect density ratio (I_D/I_G) of graphite and graphene samples calculated from Raman spectra

Sample	G	2 V	4 V	6 V	8 V	10 V
I_D/I_G	0.9719	1.0690	1.1568	1.1726	1.1337	1.1145

distinct characteristic peaks at 26.03°, 42.0°, 44.15° and 54.05 2θ values corresponding respectively to the (0 0 2), (1 0 0), (1 0 1) and (0 0 4) planes.[18] For all the exfoliated samples, a broad peak centered at the 2θ value of ~25° which is the typical diffraction signature for few layered graphene[19] was observed. Broadness of the peak suggests disordering of the initial graphitic structure

leading to a reduction in the number of stacked graphene layers in the exfoliated product. The absence of graphene oxide characteristic peak around 16° 2θ values confirms that the exfoliated samples majorly contained reduced graphene layers.

UV-visible spectroscopy refers to absorption spectroscopy or reflectance spectroscopy in the UV-visible region. The UV-visible spectrum corresponds to the absorption bands of functionalities present in a molecule. UV-vis absorption spectra obtained from graphene samples exfoliated at different potentials are shown in Fig. 3. The absorption peak at the wavelength (λ_{max}) of 270 nm which corresponds to the $\pi \rightarrow \pi^*$ transition of the aromatic C–C bonds[20] in graphene was observed for all the electrochemically exfoliated samples. The absence of absorption peak around 230 nm which corresponds to the $\pi \rightarrow \pi^*$ transition of aromatic C–C bond of graphene oxide[20] confirmed that all the exfoliated products were free from graphene oxide.

Yield of graphene as a function of potential was determined. The absorption coefficient (α) was experimentally determined in order to obtain the graphene concentration in the exfoliated graphene dispersion. Absorption coefficient is an important parameter in characterizing concentration using the Lambert–Beer law[21] ($A/l = \alpha C$ where, A is absorption peak intensity; l is path length; C is concentration and α is the absorption coefficient). Absorbance per unit path length at λ_{660} nm was measured for known concentration of graphene dispersions prepared by adding weighed amounts of graphene in water. Fig. 3(b) shows the relationship between absorption per unit length and known graphene concentrations. Slope of the straight line fit through the data points in Fig. 3(b) provided the absorption co-efficient value of $\alpha = 2090$ ml mg^{-1} m^{-1}. The unknown graphene concentration of the exfoliated samples was determined using the calculated absorption co-efficient value and the Lambert–Beer law. Concentration of graphene in the exfoliated dilute graphene dispersions were found to be 15.39 mg ml^{-1}, 21.79 mg ml^{-1}, 33.60 mg ml^{-1}, 46.97 mg ml^{-1} and 57.07 mg ml^{-1} for 2 V, 4 V, 6 V, 8 V and 10 V respectively. Yield of graphene increased with increase in the exfoliation potential.
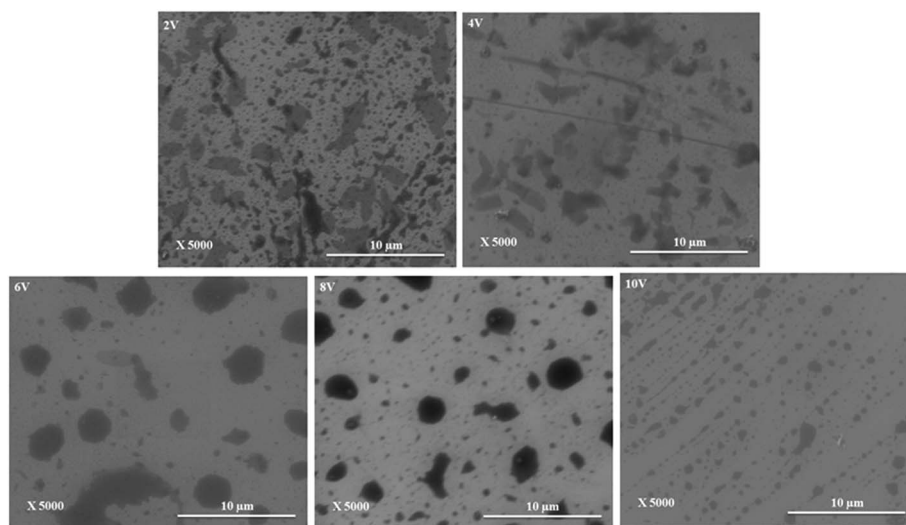

Fig. 5 SEM micrographs of graphene sheets prepared at different intercalation potential.
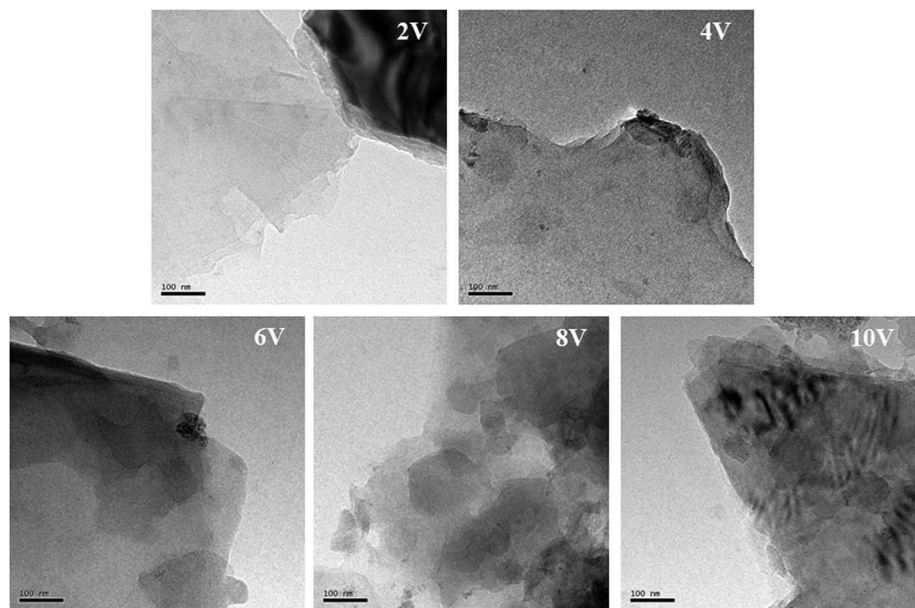
Fig. 6 TEM bright field images of graphene samples synthesized at 2 V, 4 V, 6 V, 8 V and 10 V intercalation potential.

Raman spectra obtained from graphite and exfoliated samples are given in Fig. 4. Raman spectra obtained from all the samples revealed three major peaks corresponding to D band at 1350 cm^{-1}, G band at 1590 cm^{-1}, and 2D band at 2700 cm^{-1}.[22,23] D band corresponds to the presence of sp^3 defects, G band corresponds to the phonon mode in-plane vibration of sp^2 carbon atoms and 2D band corresponds to the two phonon lattice vibration.[22,23] According to Fig. 4, a shift in the 2D band position of exfoliated graphene samples towards lower wave number as compared to the 2D band position of graphite confirms the presence of few layer graphene in the exfoliated

samples.[19] Also, an increase in the intensity of 2D band with increase in the intercalation potential indicated towards a decrease in the number of graphene layers with increase in the exfoliation potential.

Ratio of the intensity of D band (I_D) and G band (I_G) in the Raman spectrum provided information about the defect density of graphite and graphene.[24] The calculated I_D/I_G ratio of all the samples is tabulated in Table 1. The defect density of the exfoliated samples slightly increased when compared to defect density of the graphite rod which was used as the graphene source. It was surprisingly observed that, the I_D/I_G ratio
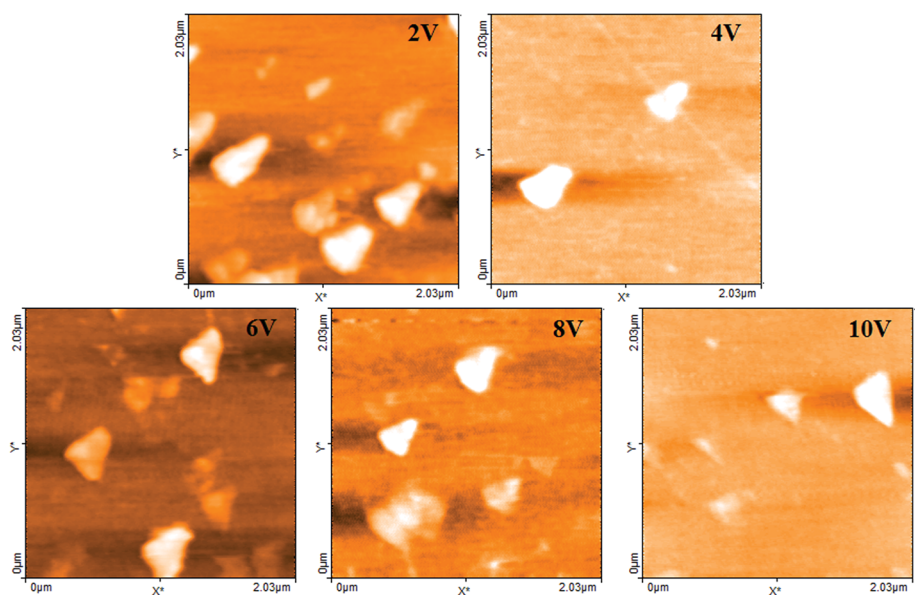

Fig. 7 AFM topographical images of graphene prepared by electrochemical exfoliation process with saccharin as an intercalating agent at different intercalation potential.

increased progressively for the samples exfoliated at 2 V, 4 V and 6 V whereas it monotonically decreased with further increase in the exfoliation potential to 8 V and 10 V. This result indicates that the defect density in the exfoliated graphene is sensitive to the exfoliation potential.

SEM micrographs of graphene samples dispersed on silica wafer are given in Fig. 5. SEM micrographs shows large, irregular and well separated graphene sheets with dimensions from nano to micron scale. Representative TEM bright field images of the exfoliated graphene samples are shown in Fig. 6. TEM images reveal the presence of isolated few layer graphene sheets in the graphene samples produced at different intercalation potentials. A representative AFM image of graphene samples synthesized using different intercalation potentials is shown in Fig. 7. The Z-height profiles obtained from several AFM images of the exfoliated samples revealed the average thickness of the graphene sheets exfoliated at 2 V, 4 V, 6 V, 8 V and 10 V to be 4.49 ± 0.86 nm, 4.10 ± 0.77 nm, 3.47 ± 0.42 nm, 3.61 ± 0.78 nm and 3.36 ± 0.65 nm respectively. For obtaining the thickness data, approximately 20 individual measurements were made for each graphene sample. The microscopic analysis clearly indicated that the as-exfoliated samples contain few layer graphene sheets.

Conclusion

In conclusion, synthesis of few layered graphene from an anodic electrochemical exfoliation process using a non-toxic and eco-friendly molecule is illustrated. Bulky and negatively charged saccharin anion was successfully intercalated into graphite anode and exfoliated by using chronoamperometry technique. XRD profile, Raman and UV-visible spectrums confirmed the presence of few layer graphene in exfoliated product. Increase in the broadness of the characteristic peak of graphene in XRD profile and increase in 2D band intensity in Raman spectra confirmed that the number of graphene layer decreased with increase in the intercalation potential. Raman spectra also illustrated that by varying the exfoliation potential the defect density of the graphene sheet can be tuned. SEM, TEM and AFM micrographs confirmed the presence of few layered graphene sheets from nano to micron dimensions.

Acknowledgements

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