

Preparation of few layer graphene sheets (FLGS) prepared by an electrochemical method

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Abstract: Graphene with two dimensional structures is a very exceptional material, since it has advantage of being excellent conducting material. Few layer of graphene sheets (FLGS) have been successfully prepared by an electrochemical method directly from graphite using oxalic acid as electrolyte. The prepared few layer FLGS have been characterized by X-ray diffraction(XRD), UV-Vis spectroscopy, field emission scanning electron microscope(FESEM), transmission electron microscope(TEM). The characterization reveals that the prepared FLGS is very good in quality. The measured current (I) vs voltage (v) shows that FLGS are highly conducting in nature. The hydrophobicity/Hydrophilicity of the prepared FLGS have been investigated for various applications.

Introduction: Since the discovery of one-atom-thick single layer of SP^2 bonded carbon atomsgraphenesheet in 2004 [1], closely packed honeycomb crystal lattice has paying attention from fundamental research and its application [2].The unique various properties such as electrical, physical, optical etc. has great application in Field-effect transistor [3,4], ultrasensitive sensors [5], electrochemical devices [6], transparent electrodes [7], different nanocomposite [8], batteries [9], supercapacitors [10] and hydrogen storage [10]. Main research focus is for the preparation of graphene in large scale with low cost due to the exotic physical properties and the predicted applications in science and technology. The methods toprepare a graphene sheets are mechanical exfoliation [1], Epitaxial growth [11], and chemical vapour deposition [12].However, the above methods are not effectively influenced of the mass production due to their low yield and high cost. There must be required another technique to produce the mass production of graphene with low cost, scalability, reproducibility, process ability and quality for the commercial application of the industrial purposes.Reduced graphene oxide(RGO) is the same like as graphene which is obtained from graphene oxide (GO) using another type of reducing agents [13,14].There are to be found heavily oxygenated by way of hydroxyl and epoxide functional groups on the surface and at the edges [15] of the obtained graphene sheet in which the electrical property is degraded.There are another method to prepare graphene straightforwardly from graphite exclusive of functional groups. This method is a one-step amalgamation of ionic-liquid-functionalized graphene sheet, also called electrochemical method [16]. In this method awful impurities for example nitrogen and water arises on the surface of graphene sheet. Highly eminence graphene was prepared by Su et al. by electrochemical exfoliation with strong sulfuric acid like as the electrolyte [17] which can smash up the honeycomb lattice throughout preparation.For the high quality few layer of graphene sheet, an electrochemical method from graphite via oxalic acid as electrolyte has been reported to avoid impurities and functional groups [18]. We have investigated the hydrophobic and hydrophilic nature of the graphene prepared by electrochemical method as reported earlier. The graphene sheets obtained in these methods do not contain any functional groups of carbon with maintaining the hexagonal structure with better electrical property.



Materials and Methods:

High quality pure graphite rod and Oxalic acid (Sigma Aldrich) and a DC voltage source.

FLGS were prepared by electrochemical method using two high quality graphite rods like electrodes and oxalic acid like electrolytes. A dc voltage of 60 V was applied to the electrodes which was immersed in the solution of oxalic acid (0.3M) maintained at 0° C about 20 hours. At first the electrodes were wetted and then the interaction of $C_2O_4H^-$ with the grain boundary of graphite were happened. After a few times, the graphite rods rust and dissociates into small pieces in the solution. The upper portion of the solution was filtered after sonication and then neutralized to recover the graphene flakes. The collected samples were dried in an oven at 130°C about 10 hours.

Result and Discussion:

The FESEM image of graphene sheets prepared by electrochemical is shown in Figure 1(a). From the FESEM images of graphene sheets, it is mainly observed that exfoliated crumpled graphene sheets are randomly oriented. The TEM image of graphene sheets are shown in Figure 1(b). A few layers of sheets through a sheet distance about 0.335nm is confirmed by the TEM images. The HRTEM image (Figure 1(c)) reveals that the prepared materials are few layers graphene sheets (FLGS). The many spots in diffraction pattern confirms the crystalline nature of FLGS (figure 1(d)).

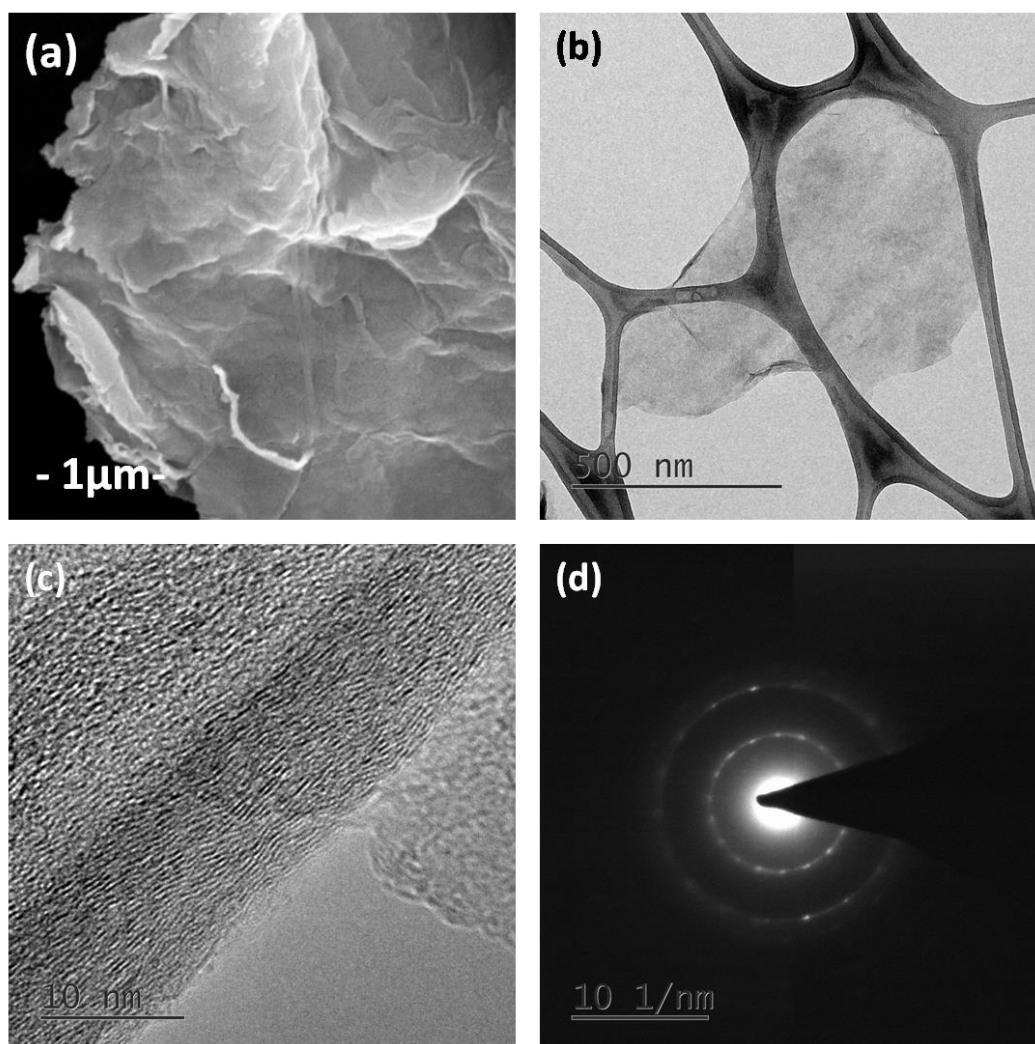


Figure1: (a) FESEM, (b)TEM, (c)High resolution TEM images, (d) SAED pattern of FLGS

The XRD pattern of FLGS shown in figure 2(a) assured the crystalline structure which shows a sharp diffraction peak at 26.148° . UV-Vis absorption spectrum of few layer of graphene sheets shown in figure 2(b) shows the absorption peak at 273 nm in relation to C=C bonds admit that there is no other functional group. Current (I) – Voltage (V) characteristics of few layer of graphene sheets is shown in the figure 2(c). The obtained higher current in FLGS is due to sp^2 conjugation in FLGS without any functional group.

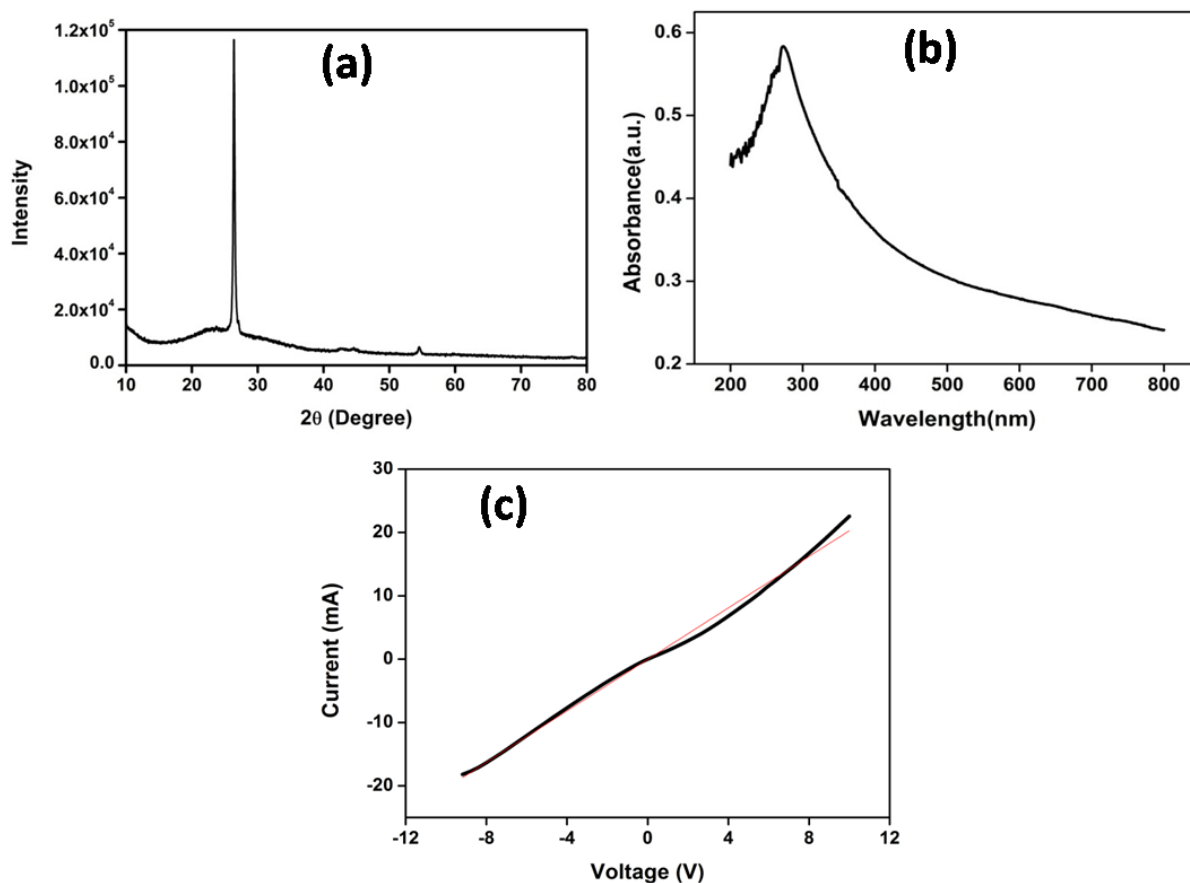


Figure 2:(a)XRD pattern, (b) UV-Vis, (c) I-V characteristics of FLGS.

The reversible wettability transition from hydrophobic to high hydrophilic nature of FLGS was accomplished by Ultraviolet (UV) irradiation and stored in vacuum [19]. The irradiation duration–dependent contact angle (CA) of water on FLGS shown in figure 3 in ambient temperature was measured by an optical Contact angle meter. According to this figure CA slowly decreases from 87.16° to 52.93° for FLGS showing to UV irradiation from 0 to 120 minutes in step of 30 minutes. Therefore the hydrophobic state can be transferred to the highly hydrophilic state under UV irradiation within 2 hour.

Then the samples were heated at 80°C for 5 hours in vacuum and measured the contact angle. Figure 4 shows the transition from hydrophilic to hydrophobic of the obtained graphene sheet. From the figure, it can be observed that the contact angle increases towards hydrophobic using vacuum storage after 5 days of the hydrophilic graphene sheet which was obtained by the UV irradiation. From the above experiment it is clearly seen that the transition from hydrophobic to hydrophilic state under UV

irradiation (2 hours) is faster than the vacuum storage (5 days). From this result, It can be suggested that after applying irradiation the transition has been occurred by the chemical adsorption before physical adsorption on graphene, as the physically adsorbed molecules desorbed within a short time. Applying UV irradiation, the chemisorptions of O_2 molecules is induced on the surface of graphene sheet. When the UV irradiation is not applying and the graphene sheet was placed in vacuum then the O_2 molecules were gradually replaced by the physically adsorbed water molecules on the surface. But there is possible transition from hydrophobic to hydrophilic and vice versa of graphene using Density Functional theory (DFT) which was already reported [20].

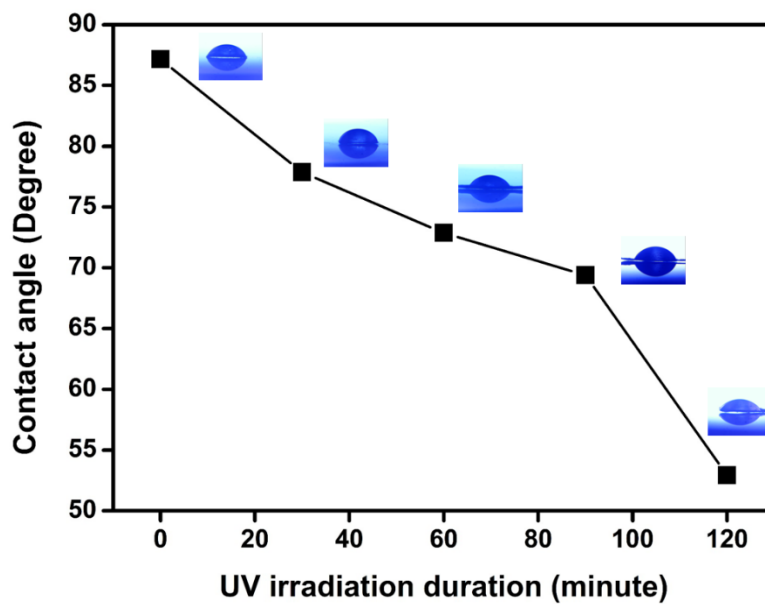


Figure 3: The contact angle of graphene with different duration of UV irradiation.

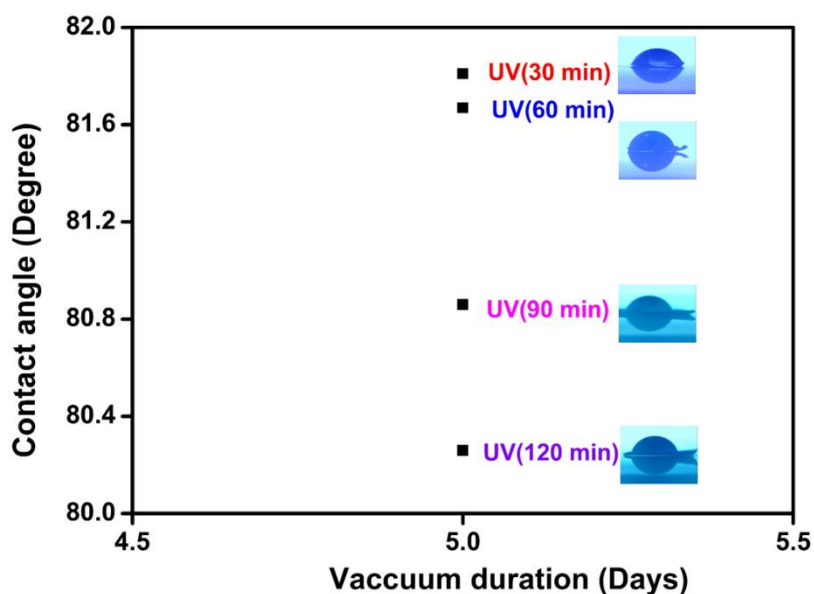


Figure 4: The contact angle of graphene sheet in the vacuum storage.

Conclusion:

Here a significant synthesis of FLGS was prepared directly from graphite by electrochemical method. From the above characterization, it is clear that the obtained FLGS are better in quality than rGO [13,14]. The transitions of graphene sheets under UV irradiation and vacuum has been observed experimentally. From hydrophobic to hydrophilic transition, it can be found that UV irradiation worked like a switch by means of the dissociative adsorption of H₂O on the graphene surface and also concluded that it can be controlled. The obtained result gives a new insights into the elemental principles of water splitting through graphene-based materials.

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