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Synthesis of graphene platelets by chemical and electrochemical route

Rajendran Ramachandran [a], Sathiyanathan Felix [a], Girish M. Joshi [c], Bala P.C. Raghupathy [a,d,*], Soon Kwan Jeong [b,**], Andrews Nirmala Grace [a,b,***]

[a] Centre for Nanotechnology Research, VIT University, Vellore 632014, Tamil Nadu, India
[b] Climate Change Technology Research Division, Korea Institute of Energy Research, Yuseong-gu, Daejeon 305-343, South Korea
[c] Materials Physics Division, School of Advanced Sciences, VIT University, Vellore 632014, Tamil Nadu, India
[d] Research & Advanced Engineering Division (Materials), Renault Nissan Technology & Business Center India (P) Ltd., Chennai, Tamil Nadu, India

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ABSTRACT

Graphene platelets were synthesized from graphene oxide by chemical and electrochemical route. Under the chemical method, sodium borohydride and hydrazine chloride were used as reductants to produce graphene. In this paper, a novel and cost effective electrochemical method, which can simplify the process of reduction on a larger scale, is demonstrated. The electrochemical method proposed in this paper produces graphene in powder form with good yield. The atomic force microscopic images confirmed that the graphene samples prepared by all the routes have multilayers of graphene. The electrochemical process provided a new route to make relatively larger area graphene sheets, which will have interest for further patterning applications. Attempt was made to quantify the quantum of reduction using cyclic voltammetry and choronopotentiometry techniques on reduced graphene samples. As a measure in reading the specific capacitance values, a maximum specific capacitance value of 265.3 F/g was obtained in sodium borohydride reduced graphene oxide.

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1. Introduction

Graphene materials have recently attracted much attention among the researchers [1], due to its unique optical, mechanical, thermal and electronic properties [2,3]. Applications of graphene based materials range from energy storage [4], transparent conducting films [5], sensors [6], electromagnetic shielding [7] to nanocoolants [8]. Graphene has been synthesized by both top down and bottom up approaches like mechanical cleavage, and chemical vapor deposition [2], respectively. Another popular and cost effective method is by chemical modification of natural graphite [9]. In general, graphite is oxidized using one of the established methods: Brodie's method using potassium chlorate and fuming nitric acid [10], Staudenmaier method using concentrated sulphuric or nitric acid and chlorate [11], or Hummer's method using potassium permanganate and sulphuric acid [12] to form graphene oxide (GO). Hummer's method is popular as it is less hazardous and is less time consuming with higher yields. Hummer's method involves treatment of graphite with potassium permanganate and sulfuric acid, which leads to intercalation of large amount of oxygen molecules in between the graphene layers. GO is generally insulating and has limited applications [13]. On the other hand, reduced GO is useful as a 2D conductor with numerous applications. The reduction is a critical process which has been carried out by chemical methods using different reducing agents such as hydrazine [14], sodium borohydride [15] and ascorbic acid [16]. The other methods involved are thermal reduction [17], electrochemical method [18] and more recently using ultra-violet treatment [19].

The efficiency of reduction varies amongst the different methods which can be characterized using UV–vis spectroscopy, X-ray diffraction and FT-IR spectroscopy. In this paper, two different methods have been explored for the reduction process of graphene oxide to graphene viz. chemical and electrochemical. In the former route, two reducing agents viz. sodium borohydride and hydrazine chloride have been used and for the electrochemical part, chronoamperometry technique was done in a dialysis membrane to get graphene powders. The novel route to use dialysis membranes gained inspiration from the barrel plating concept widely used in electroplating industry [20] and recent work by Zhou et al. [18], on electrochemical reduction of GO.

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* Corresponding author at: Renault Nissan Technology & Business Center India (P) Ltd., Chennai, Tamil Nadu, India.
** Corresponding author at: Climate Change Technology Research Division, Korea Institute of Energy Research, Yuseong-gu, Daejeon 305-343, South Korea.
Tel.:+82 42 860 3367; fax:+82 42 860 3134.
E-mail addresses: balapraveen2000@yahoo.com (Bala P.C. Raghupathy), jeongsk@kier.re.kr (S.K. Jeong), anirmalagrace@vit.ac.in, anirmalagladys@gmail.com (A.N. Grace).
***Corresponding author at: Centre for Nanotechnology Research, VIT University, Vellore 632014, Tamil Nadu, India. Tel.: +91 416 2202412; fax: +91 416 2243092.

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However, the amount of GO that can be reduced and obtained as a powder for further use remained less in all the work reported so far [21,22]. The electrochemical exfoliation process reported was especially useful in making dispersions and not for making graphene layers [23]. Though papers are reported on the electrochemical production of graphene, the work is limited to thin film growth on substrates. In this work, graphene is produced by electrochemical route as powders with good yields and is economically very cheap. The current developed method can be used to prepare large quantities of reduced graphene oxide (RGO) from the commercial point of view without the use of hazardous chemicals and high pressure.

2. Materials and methods

2.1. Materials

Graphite powder, AR grade sodium nitrate, potassium permanganate, sulfuric acid, sodium borohydride, hydrogen peroxide and hydrazine chloride were purchased from S.D. Fine Chem. Ltd., Mumbai, India and were used as received.

2.2. Preparation of graphene oxide (GO)

Graphene oxide was synthesized from natural graphite powder through modified Hummer's method [24]. Graphite powder (0.5 g) and sodium nitrate (0.5 g) was mixed with 23 ml of concentrated sulfuric acid (98% pure) and the mixture was kept in an ice bath for 4 h under stirring. Potassium permanganate (3 g) was then added into the mixture. The reaction mixture was maintained at 35 °C for 2 h with continuous stirring and further diluted with 46 ml of water. Then, the temperature was raised to 98 °C and maintained for another 2 h. The heating was switched off and the reaction mixture was diluted with 100 ml warm water and 10 ml of hydrogen peroxide. After 1 h of stirring, the solution turned light yellow in color, which was repeatedly washed and centrifuged in distilled water to get GO. Finally the powder was dried at 60 °C for 24 h.

2.3. Sodium borohydride based reduced graphene oxide (SRGO)

SRGO was prepared from graphite oxide according to the literature [25]. GO (30 mg) was dispersed in water (30 ml) in an airtight container of 60 ml capacity. To it was added sodium borohydride (0.04 M) and 5 ml of 1 M sodium hydroxide solution. Finally, the mixture was kept at 90 °C for 1 h and separated by centrifugation. The as obtained powder was dried at 60 °C for 24 h.

2.4. Hydrazine chloride based reduced graphene oxide (HRGO)

GO (30 mg) and hydrazine chloride (0.05 M) was taken in an airtight container containing 30 ml of water. This mixture was kept at 90 °C for 1 h. After 1 h, the mixture was centrifuged at 7500 rpm and the powder was dried at 60 °C for 24 h.

2.5. Electrochemically reduced graphene oxide (ERGO)

Electrochemical reduction of graphene oxide was performed by using electrochemical work station. Glassy carbon, Pt wire and Ag/AgCl were used as the working, counter and reference electrodes, respectively [18]. Sodium phosphate buffer solution (NaPBS, 1 M, pH 4.10) was used as the electrolyte. GO (0.5 g) was taken in a dialysis membrane (Himedia, MWCO-12 kDa). The GC electrode was put into the membrane and kept tied with a thread. The experimental set up is shown in Fig. 1. Chronoamperometry (CA) was carried out at a potential range of -0.9 V to -1.0 V for 4000 s. Finally the powder was centrifuged and dried at 60 °C for 24 h.

2.6. Electrochemical measurements

The cyclic voltammetry experiments were investigated by using CHI 600C electro chemical work station in a three electrode system. Carbon paper, Ag/AgCl, and platinum electrodes were used as working, reference and counter electrode, respectively. The working electrode was coated with 1 mg of active material (G/GO/RGOs) dispersed in 2 μl nafion solution. The experiments were operated at room temperature with 1 M KCl electrolyte at different scan rates in the potential range from -0.2 V to 0.8 V.

2.7. Material characterization

X-ray diffraction system (BRUKER, D8 Advance, Germany) was used for the X-ray analysis with Cu-Kα radition (λ = 1.540 Å). Step scanning was done with 2θ intervals from 8° to 60°. The AFM images were taken from the system (Nanosurf EasyScan 2 AFM, version 1.3). UV–vis spectroscopy (JASCO, V-670 spectrometer) was used for the measurement of absorbance to fine the electronic structure of the samples in the wavelength range of 200–800 nm. Fourier transform infrared spectra were recorded using spectrum one: FTIR-spectrometer in the range 450–4500 cm^{-1} to characterize the functional groups. The morphology and distribution of the graphene layers was studied by optical microsope (Olympus, BX61-33Mu). The electrochemical analyzer (CHI 600 C work station, version 5.01) was used for cyclic voltammetry and chronoamperometry measurements. The morphology of the materials was investigated using FEI Quanta FEG 200 SEM instrument. The settling tests of the samples were recorded by ultrasonication at different time durations.

3. Results and discussion

The protocol for the electrochemical reduction of GO to graphene is explained in the previous section. A schematic of the electrochemical method is given in Fig. 1. As can be seen from the schematic, the graphene oxide flakes are tightly packed within the dialysis membrane. The dialysis bag, functions as an ion/electrolyte transporting media whilst retaining the graphene platelets. It should be noted that the material inside the bag should be held tightly so that the platelets physically touch each other and maintain electrical connectivity between them. Chronoamperometry technique was used for the reduction of GO to graphene at a potential range of -0.9 V to -1.0 V for 4000 s. This was done in 1000 s pulse at the said voltage. Fig. 2 shows the typical choronoamperometric result for the electrochemical reduction of graphene oxide in PBS buffer electrolyte. As seen in the figure, the current increased rapidly and decreased after about 500 s indicating the possible reduction of graphene oxide. After 1000 s, the current increased at every pulse time (1000 s) indicating the restoration of π network in the carbon structure [18]. This was further confirmed from the color change in the GO and ERGO solution. The yellowish brown color solution turned light black after electrochemical reduction indicating the reduction of GO (marked 4 in Fig. 3). Similarly, under the chemical methods, reductants like $NaBH_4$ and hydrazine chloride were used to prepare graphene as explained in the previous section, where a formation of black color indicated the reduction of GO to graphene.

Fig. 3a–d shows the photographic image of graphite, GO, SRGO, ERGO and HRGO solutions as a function of sonication time prepared by various routes. In Fig. 3a, the GO solution in water medium was brownish yellow in color confirming the oxidation of graphite to GO as compared to graphite (G). After reduction of GO

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