

Hydroxy-Functionalized Graphene: A Proficient Energy Storage Material

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Abstract

The present exploration emphasizes on the fabrication of graphene sheets with optimum hydroxy (-OH) functionalities which would establish tuned electrical charge storage capacity thereby revealing appreciable electrochemical signature. Compared to other available chemical procedures, here we have adopted a simple, facile-one-pot sonochemical route for the synthesis of the material: Hydroxy-Functionalized Graphene (hG), starting from pristine graphite powder. The as-synthesized sample was characterized using FTIR, XPS, TGA and FESEM techniques which prompted formation of hydroxyl-functionalized graphene. We further investigated the electrochemical performances using techniques such as cyclic voltammetry and chrono-potentiometric charging/discharging cycles. The material shows potential applications in energy storage devices.

Keywords: Hydroxy-functionalized graphene; Electrochemical performances; Specific capacitance; Energy storage applications

Introduction

The ever rising demands of energy have encouraged the urge for promising electrochemical energy storage systems. The “Supercapacitors”, due to their enhanced power supply capacity, longevity, and high charge propagation dynamics have emerged as one of the most challenging field for research and development community [1,2]. As far as the electrode materials for “supercaps” are concerned, current research is immensely focusing on carbon-based materials [3-5] due to their abundancy, ecofriendliness and easy processibility. Among them, graphene has incurred extreme interest due to vast array of unique and highly desirable electronic as well as electrochemical properties it offers, comes the most promising prospects when implementation within areas of energy research is sought [6-8]. The use of graphene as supercapacitor material has been widely reported for the past few years, with numerous studies also reporting that graphene to be a far advanced super-capacitor material than existing carbon and polymer based materials [9,10]. For “supercaps”, the key to improve “specific capacitance” is to enhance the specific surface area and control the pore size, layer stacking, and distribution of the electrode material, as investigated by Du et al. [11]. The authors reported GNSs with a narrow mesopore distribution of ~ 4 nm from natural graphite via oxidation and rapid heating processes, and found to maintain a stable specific capacitance of 150 Fg⁻¹ under the specific current of 0.1 Ag⁻¹ for 500 cycles of charge/discharge. Wang et al. [12] also investigated graphene as a potential super-capacitor electrode material, where a maximum specific capacitance of 205 Fg⁻¹ was measured with a power density of 10 kWkg⁻¹ at a energy density of 28.5 Whkg⁻¹, excellent cyclic ability was obtained also with ~90% specific capacitance remaining after 1200 cycles. Interestingly, other work [13] has shown that using an electrophoretic deposition method to deposit GNSs onto nickel foams with three-dimensional porous structures, the high specific capacitance of 164 Fg⁻¹ is obtained from cyclic voltammetric (CV) measurement at a scan rate of 10 mVs⁻¹, and it was noted that after 700 cycles the specific capacitance remains 61% of the maximum capacitance. Yet further exciting prospects emerge where graphene prepared via graphitic oxide in an ionic liquid medium, exhibited a specific capacitance and energy density of ~75 Fg⁻¹ and 31.9 Whkg⁻¹ respectively at operating voltage of 3.5 V [14]. Here, the authors have claimed that the obtained energy density is one of the highest values reported till date, inferring

that the performance characteristics of graphene are directly related to its advanced quality in terms of numbers of graphene layers and the inherent surface area. Thus, the above survey suggests the true potentiality for graphene systems as electrochemical capacitors, but their scalability might be an issue. However, it is also evident that the general specific capacitance of graphene is not as high as expected, and thus it is notable that many researchers have started to incorporate/modify graphene through different functionalization in pursuit for improved capacitance performances [15].

Recently graphene oxide has been found to show greater charge storing capacity than graphene but it has limitations of poor electrical conductivity compared to graphene [16]. Hence, an optimization of oxygen content on graphene sheets may assist in tuning both conductivity as well as charge storage in the system. Hence, in the present exploration, we have controlled the extent of oxidation of graphite to obtain the proportionate oxygen functionality to achieve tunability in electronic properties so that the system can be used as an effective electrode material for near future carbo-supercapacitors. In addition, we have adopted a very simple, facile, cost effective, green one pot sonochemical technique to obtain the desired material which is found to be a very competitive electrode material for “supercaps” in the near future technology.

Experimental Details

The method of synthesis of hG is facile; green as well as cost effective. The aid of sonochemical energy delivers necessary activation energy for the formation of hG by oxidant ammonium peroxodisulphate ion, which oxidizes individual graphite layers to hydroxy-functionalized graphene [17]. When graphite (2.5 g/lit) is subjected to ultrasonic energy in presence of aqueous ammonium peroxodisulphate (10 g/

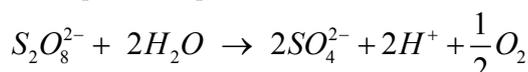
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lit), the large peroxydisulphate ions intercalate and oxidize the graphite layers to form hydroxy functionalized graphene (h-GO). The aid of ultrasonication helps in fragmenting and exfoliating large sheets of graphite layers into smaller thinner layers of sheets as well as imparting necessary activation energy for e-transfer to form h-GO. Since the rate of oxidation is slower compared to other conventional stronger oxidants like perchlorates or permanganates, the specificity of the reaction is high and over-oxidation is restricted [18]. Thus we obtain hydroxyl functionality as major product compared to traditional over oxidation product with large proportions of =C=O, -COOH functionalities on the surface of the individual graphene sheets. The oxidation process by ammonium peroxydisulphate stands on the reaction:



The obtained product was then repeatedly washed with double-distilled water and the n dried at 90°C. The as-synthesized sample was characterized using powdered-XRD, FTIR, TGA, HRTEM, FESEM techniques. Electrochemical performances were investigated using techniques such as cyclic voltammetry and galvanostatic charge/discharge cycles with graphite carbon electrode (diameter = 1.3cm, sample deposited on electrode = 10µl of 0.5 mg/ml) as Working Electrode, with 1(M) Na₂SO₄ aqueous solution as electrolyte, Pt wire as Counter Electrode and SCE as Reference Electrode respectively.

Results and Discussion

Figure 1A shows the FTIR spectrum of hG sample and pristine graphite. The peaks at 3433 and 3135 cm⁻¹ (free O-H as well as hydrogen bonded O-H stretchings), 2938 and 2852 cm⁻¹ (=C-H stretch, C-H stretch) 2604-2497 cm⁻¹ (H-C=O: C-H stretch) 1719 cm⁻¹ (C=O stretch) 1641 cm⁻¹ (-C=C- stretch C-C stretch (in-ring)) 1408 cm⁻¹ (C-C stretch (in-ring)) 1224 cm⁻¹, 1181 cm⁻¹ (C-O stretch alcohols, carboxylic acids, esters) 1060 cm⁻¹ (C-O stretch) 1005 cm⁻¹ (C-H bendings), < 1000 cm⁻¹ (aromatic region) well establish the functionalization of graphene compared to graphite [19]. Moreover, the existence of very weak peak at 1745 cm⁻¹ asserts the presence of very little proportion of C=O of carbonyl and carboxylate functional groups in the material. So, we can conclude that the main oxygen containing functional groups is hydroxy (-OH) groups in our hG sample. Hence, formation of hydroxy functionalized graphene (hG) is hereby indicated.

To study the thermal stability of the as-synthesized sample, we carried out thermogravimetric analysis (Figure 1B) of hG sample and compared it with its parent graphite. The hG sample has lower thermal stability and its decomposition is similar to functionalized graphenes available in the literature. As expected, graphite was highly stable throughout the entire range of temperature study. Three step decompositions are observed for hG sample. The apparent mass reduction at ~ 100°C is due to loss of loosely bound water inside the structure. Again the mass loss at around 350°C was caused by pyrolysis of the oxygen-containing for elimination of remaining functional groups. Normally this decomposition starts at around 200-250°C for other systems reported but in our case as the hydroxy/ epoxy groups are supposed to be linked by hydrogen bonds, as result of which the loss commences at higher temperature [20]. Further decomposition takes place at around 500°C where almost 30% mass loss due to skeletal carbon loss. The above results thus indicate that functionalization has led to exfoliated graphene sheets which in-turn reduces the thermal stability for the exfoliated hG sample compared to the parent material, graphite.

Further, XPS has been used in the detection of the different oxygen-

containing functional groups that form on the carbon surface during the chemical oxidation process of graphite. Figure 1C presents the typical C1s spectra of hG sample. The C1s signal shows that the C1s spectra yields peaks with different binding energy values representing carbon in the non-oxygenated C-C or C-H (284.3 eV), C=C (285.5 eV), epoxy/single C-O bonds/C-OH (286.4 eV) [21]. The peaks for double C=O bonds (carbonyl, 287.1 eV), and carboxylic COOH or O-C=O (288.5eV) are almost negligible signifying that epoxy/hydroxy (terminal) functionalized graphene has been preferentially obtained by this synthetic route.

Figures 1D and 1E shows the SEM images of graphite and hG samples respectively. The morphology of the pristine graphite sample shows thick, gigantic sheet structures. However, on functionalization/exfoliation in hG sample, the dimension of the sheets gets considerably reduced as well as more crumpled. Functionalization of graphene sheets imparts defects on the sheets which lead to such morphological alterations compared to the parent structure.

Thus from the above characterization studies it is evident that we have successfully synthesized hydroxy-functionalized graphene. Moreover, compare to the parent, the hG samples have a more enhanced surface area as evident from the SEM images. Accordingly, we opted for electrochemical studies to investigate its capability as electrode material for supercapacitors.

Electrochemical studies: CV and CD

To explore the potential applications in electrochemical capacitors, the hG sample was used to make supercapacitor electrodes and characterized with cyclic voltammetry (CV) and galvanostatic charging/discharging (CD) measurements.

Figure 2A shows the CV of the hG sample at different scan rates respectively in the potential range 0.0 V to +1.0 V vs. SCE. The CV profiles are almost rectangular shape for double layer capacitance, which suggested that the capacitance of the material is primarily originating from non-Faradic redox reactions. Thus, electrochemical double layer charge storage mechanism is being indicated in this case. The specific capacitance of the electrode can be calculated from the CV curves according to the following equation [22],

$$C_m = \frac{i}{mv}$$

Where, *m* is the mass of electroactive material, *v* is the potential sweep rate, and *i* is the even current response defined by (*V_a* and *V_c* represent the lowest and highest voltages, respectively) and obtained through integrating the area of the curves,

$$i = \int_{V_a}^{V_c} i(V) \frac{dV}{(V_c - V_a)}$$

The specific capacitance of hG sample calculated from CV curves was 161 Fg⁻¹ measured at the scan rate of 2 mVs⁻¹, this obtained value being appreciable in the voltage range [11-13].

Figure 2B shows the charging-discharging behavior of the hG sample. Additionally, galvanostatic constant current charge-discharge curves at various current densities were performed with an electrochemical window of the potential range 0.0 V to + 1.0 V to further examine the electrochemical performance of the material. The charging-discharging curves are almost linear and somewhat mirror symmetrical which suggests good electrochemical performance for hG sample. The specific capacitance of the sample can be calculated from the GC curves using the following equation: [22,23].

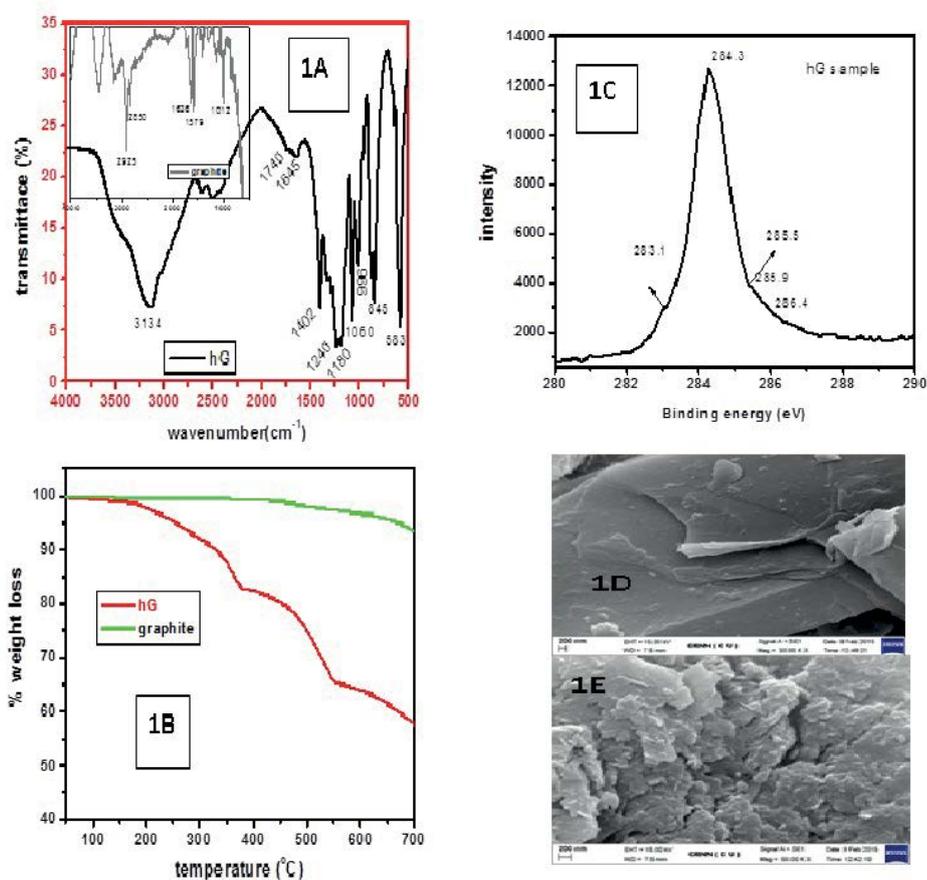


Figure 1: A. FTIR spectrum of hG sample and pristine graphite. B. Thermogravimetric analysis of hG sample in comparison with parent graphite. C. Typical C1s spectra of hG sample. D. SEM images of graphite. E. SEM images of hG.

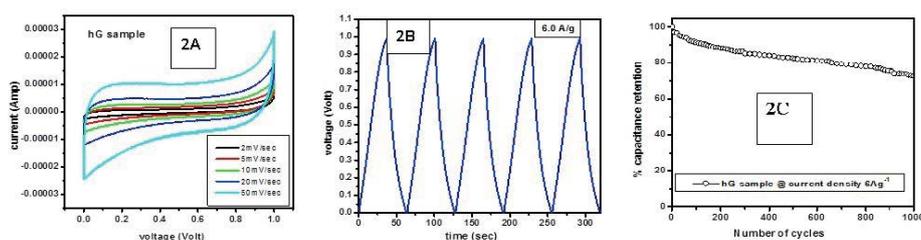


Figure 2: A. FTIR spectrum of hG sample and pristine graphite. B. Thermogravimetric analysis of hG sample in comparison with parent graphite. C. Typical C1s spectra of hG sample. D. SEM images of graphite. E. SEM images of hG.

$$C_m = \frac{I \Delta t}{\Delta V m}$$

where I , Δt , ΔV , and m denote current density, discharge time, potential range in discharge after the IR drop, and the active weight of the electrode material, respectively. The specific capacitance value was 191F/g at current density of 6Ag⁻¹, which lies in good agreement with the CV results.

In order to evaluate cycle performance of the samples, charging/discharging profiles have been conducted for 1000 cycles at the current

density of 6Ag⁻¹, which the results have been depicted in Figure 2C. We observed the capacitive retention for the hG sample was about 72%, which is quite appreciable compared to the reports available in the literature.

Conclusion

Thus, in the present work, hydroxy-functionalized graphene has been successfully prepared by a simple, green and wet-chemical method with the aid of ultrasonic energy. The obtained electrode material exhibited an appreciable specific capacitance and stable cycling performance for supercapacitor applications. Considering the significant factors such as low cost, abundant resources, simplicity of the preparative method and improved electrochemical properties, it

is obvious that hydroxy-functionalized graphene is well suitable to be considered as promising electrode material for energy storage devices.

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