



# Effect of reducing agent on graphene synthesis and its influence on charge storage towards supercapacitor applications <sup>☆</sup>



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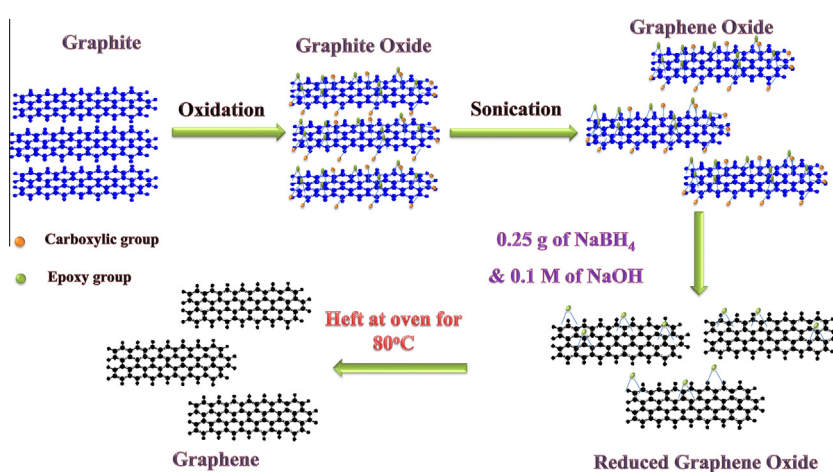
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## HIGHLIGHTS

- Chemical reduction route was adopted for graphene preparation.
- Electrochemical measurements were carried out in 6 M KOH.
- Better electrochemical properties obtained for graphene than graphene oxide.
- A high specific capacitance of 284.3 F/g was observed for SR1:10.

## GRAPHICAL ABSTRACT



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## ABSTRACT

A simple chemical route was adopted for the preparation of graphene by chemical reduction route using sodium borohydride ( $\text{NaBH}_4$ ) as a reducing agent. A systematic study was done to show the effect of  $\text{NaBH}_4$  on the reduction and the obtained graphene samples were characterized using X-ray diffraction, Fourier transform spectroscopy, Raman spectroscopy, Atomic force microscopy and High resolution transmission electron microscopy. Better reduction of GO was observed at GO and  $\text{NaBH}_4$  ratio of 1:10 (denoted as SR1:10). Further, the investigation was emphasized to show the effect of the above GO to reductant ratio on its charge storage properties. Electrochemical measurements were carried out in 6 M KOH electrolyte and the results show that the capacitance performance was increased in the order of  $\text{GO} < \text{SR1:8} < \text{SR1:4} < \text{SR1:12} < \text{SR1:10}$ . A high specific capacitance of 284.3 F/g was observed for SR1:10 electrode at 5 mV/s scan rate could be due to better electrical conductivity of sample. The ratio of GO and  $\text{NaBH}_4$  was optimized to 1:10 for high degree reduction of graphene, which has higher capacitance towards supercapacitor applications.

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## 1. Introduction

Energy storage devices such as batteries, fuel cells and supercapacitors that possess both high power density and energy densities with excellent cycling ability is a subject of immense interest due to its wide usage in portable electronic devices, electric vehicles and hybrid electric vehicles [1–4]. Among the various energy storage devices, supercapacitors are considered as a promising candidate for next generation power devices due to their advantages of fast charging/discharging and high power density [5]. A supercapacitor stores energy using either absorption of ions called electric double layer capacitors (EDLCs) and fast faradic reaction called pseudocapacitors. These two mechanism can function simultaneously, depending on the nature of the electrode materials [6]. Different carbon based materials such as activated carbon, carbon nanotube, carbon aerogel and carbon nanofibres have been studied as electrodes in EDLCs [7]. In recent years, one atom-thick layered crystalline with honeycomb structure of  $sp^2$ -bonded carbon called graphene is a good candidate for supercapacitors electrode material due to its superior electrical conductivity ( $\sim 10^6 \text{ S cm}^{-2}$ ) [8], high surface area ( $2630 \text{ m}^2 \text{ g}^{-1}$ ) [9], thermal conductivity ( $5000 \text{ W m}^{-1} \text{ K}^{-1}$ ) [10]. In addition, it can minimize the contact resistance between the electrode and current collector, unlike the case of carbon nanotube [11]. Several synthetic routes have been established to prepare graphene such as mechanical exfoliation, chemical vapor deposition, epitaxial growth on SiC and chemical route. In the chemical route, graphite oxide is prepared from graphite source with strong oxidizing agents thus weakening the Van der Waals forces between the graphene layers. Apart from this conventional route, graphite oxide have been reduced by using reducing agents at high temperatures and this chemical route is more effective for large scale synthesis of graphene, leading to the development of devices on a commercial scale. Different reducing agents like hydrazine hydrate [12], hydroquinone [13], dimethylhydrazine [10], ascorbic acid [14] and sodium borohydride [16] have been used to obtain graphene from graphite oxide precursor. A specific capacitance in the range of  $100\text{--}200 \text{ F g}^{-1}$  was obtained for graphene synthesized by different chemical routes, which is attributed to the difference in structure and surface area of graphene. The type of reducing agent and solvent always play a major role deciding the effective surface area and agglomeration of graphene sheets, which leads to better capacitive performance. Though hydrazine hydrate is a well-known reducing agent to for GO, this approach provides high sheet resistance and also causes toxic effect [15]. More effective reduction using  $\text{NaBH}_4$  has been reported by Hyeon-Jin Shin et al. The reduction level generally depends on the concentrations of reducing agent.

In this view, the present work is reported on the reduction of graphene oxide using different concentrations of  $\text{NaBH}_4$  and further its supercapacitive performance has been detailed. A systematic investigation is done to probe the role of reductant concentration towards its capacitance. The electrochemical measurements showed the better capacitive behavior of graphene, at a particular concentration of GO. A detailed mechanism to suffice our results has been given.

## 2. Materials and methods

### 2.1. Materials

AR grade graphite powder, potassium hydroxide, sodium nitrate, potassium permanganate, sulfuric acid, sodium borohydride, hydrogen peroxide and hydrazine chloride were purchased from Sigma Aldrich. All the solutions were prepared by de ionized water.

### 2.2. Graphene preparation

Graphene oxide and graphene were prepared according to our previous report [16]. In brief, graphene was prepared by the following procedure. GO (0.040 g) was dispersed in water (40 ml) and taken in an airtight container. Sodium borohydride (0.4 g) and 5 ml of 1 M sodium hydroxide solution were added into the above dispersed solution. The mixture was kept at  $95^\circ \text{C}$  for 1 h and centrifuged at 7500 rpm with de ionized water and dried at  $60^\circ \text{C}$  for 24 h. The as obtained final powder was named SR1:10. In similar way, other samples like SR1:4, SR1:8, SR1:12 were prepared by varying the concentration of sodium borohydride viz. 0.16 g, 0.32 g, 0.48 g respectively.

### 2.3. Materials characterizations

X-ray diffraction system (BRUKER, D8 Advance, Germany) was used for the X-ray analysis with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.540 \text{ \AA}$ ). Step scanning was done with  $2\theta$  intervals from  $10^\circ$  to  $60^\circ$ . Fourier transform infrared spectra were recorded using Spectrum one: FTIR-spectrometer in the range  $450\text{--}4500 \text{ cm}^{-1}$  to characterize the functional groups of the samples. Raman studies of samples were performed in a JY-1058 Raman spectrometer. The surface morphologies of samples were characterized by using High resolution Transmittance Electron microscope (JEOL 2011) and EDX mappings of the samples were obtained with FESEM by using a Hitachi S-4800. The AFM images were taken from the system (Nanosurf EasyScan 2 AFM, version 1.3).

### 2.4. Electrical conductivity measurements

Electrical conductivity of graphene oxide and graphene samples were measured using four probe set up (Model- DFP 02) at different temperatures. The active material was pelletized with a thickness of 0.45 mm and radius 6.25 mm.

### 2.5. Electrochemical measurements

All the electrochemical measurements were carried out with an electrochemical analyzer (CHI 600C work station, version 5.01) using a three electrode system in 6 M KOH as electrolyte solution under ambient conditions. The potentials and current were measured with respect to  $\text{Ag/AgCl}$  (sat.KCl) as the reference electrode. Carbon paper (Purchased from Cabot, USA) and Pt wire were used as the working and counter electrodes respectively. The cyclic voltammetry measurements were performed at various scan rates in the potential range from  $-0.2$  to  $0.2 \text{ V}$ . The working electrode was prepared as follows: In brief, a known amount of the active material was dispersed in 5 wt% of nafion and the mixture was coated on a carbon paper ( $3 \text{ cm} \times 1 \text{ cm} \times 0.1 \text{ cm}$ ). The mass of the active material on electrode was  $2 \text{ mg/cm}^2$ . Then, the electrode was dried for 3 h at room temperature.

## 3. Results and discussion

A schematic diagram (Scheme 1) is given, which shows the formation of graphene oxide and the reduction process of GO to graphene. As detailed in the experimental section, different graphene samples were synthesized at various loadings reductant and the samples were analyzed. Fig. 1 shows the XRD pattern of graphene reduced by different concentrations of  $\text{NaBH}_4$ . The interlayer spacing of graphene oxide was calculated to be  $8.8 \text{ \AA}$  at a  $2\theta$  value  $10.2^\circ$  (Fig. S1). The larger interlayer spacing of graphene oxide than pristine graphite ( $3.3 \text{ \AA}$ ) has been attributed to the intercalation of the oxygen functional groups like hydroxyl, epoxy and carbonyl during

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