

## Supercapacitor Application of Powder Prepared Using the Hydrogenation Disproportionation Desorption and Recombination (HDDR) Process in Graphene Oxide

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**Abstract.** Graphene (G) has been attracted great interest for its excellent electrical properties. However, the large-scale production of graphene is presently unfeasible. Graphene oxide (GO) can be (partly) reduced to graphene-like sheets by removing the oxygen-containing groups with the recovery of a conjugated structure. It can be produced using inexpensive graphite as raw material by cost-effective chemical methods. Although hydrogen (mixed with argon) at high temperature (1100°C) has been employed to reduce GO powder, the hydrogenation disproportionation desorption and recombination (HDDR) process in particular was unreported for this purpose. In the present work, attempts of reducing GO powder using the HDDR process have been carried out and investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM) thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FTIR). The experimental results of processing graphene oxide powder using unmixed hydrogen at moderate temperatures (about 850°C) and relatively low pressures (<2 bars) have been reported.

### Introduction

Graphene has been reported to have a high electrical conductivity [1]. Reduction of graphene oxide (GO) is a necessary processing step to improve the electrical conductivity for practical supercapacitors applications [2]. The specific capacity has been improved from 189 to 276 Fg<sup>-1</sup> with this procedure [3]. Similarly, the current density increased from 50 to 100 mA g<sup>-1</sup> with twice as much the life cycles (from 5,000 to 10,000) in these materials [3]. The reduction methods for GO material are carried out using a chemical reagent reduction or by thermal annealing although many other methods have also been employed [4-6]. The reduction temperature and the annealing atmosphere are crucial for the thermal annealing reduction of GO [4,7]. Temperatures as low as 200°C and as high as 1100°C have been employed for producing supercapacitor materials [8]. The thermal reduction process can be carried out under vacuum or a protection gas in order to cut off the oxygen gas rapidly generated on high temperature processing [4]. It has been suggested that thermally reducing GO sheets at 1000 °C under high vacuum (<10<sup>-5</sup> Torr) as the fresh reduced GO easily reacts with the residual oxygen functional groups [4]. This thermally reduced GO has a low sheet resistance about 10<sup>2</sup> –10<sup>3</sup> Ω sq<sup>-1</sup>. An inert gas has been reported to facilitate the reduction process and H<sub>2</sub> introduced to the thermal reduction process lower the processing temperature [4]. A gas mixture of Ar/H<sub>2</sub> (1:1) thermally reduces GO sheets at 450°C in 2 h [4]. The reduced GO sheets shown a high electrical conductivity of about 1×10<sup>5</sup> Sm<sup>-1</sup> (with a C/O ratio of 14.9) [4]. The HDDR process, with a distinct treatment cycle from previously reported for GO, has been employed to refine the structure of rare earth based materials [9-13]. The HDDR process uses relatively low temperatures and H<sub>2</sub> pressures and has not been applied to GO for supercapacitors applications. This paper reports for the first time the results of a work carried out on a study of HDDR GO material for supercapacitors. Electrical, compositional and morphological evaluation of the supercapacitor materials has been carried out.

## Experimental

Graphene oxide was prepared using a modified Hummers' method [15]. Graphite powder,  $\text{NaNO}_3$  and  $\text{H}_2\text{SO}_4$  were briefly stirred in an ice bath.  $\text{KMnO}_4$  was then gradually added and the temperature was kept at about  $35^\circ\text{C}$  for one hour. Subsequently, deionized (DI) water was added followed by  $\text{H}_2\text{O}_2$  (30%) turning the color of the solution from dark brown to yellow. The product was washed with DI water,  $\text{NaOH}$  (1M) and  $\text{HCl}$  (1M) until pH 7. All the work up steps were followed by centrifuging the sample at 12,000 rpm for 10 minutes. GO samples were dispersed in ethanol and exfoliated using an ultra-sonicated and dried for further analysis. This starting GO material was characterized using Raman spectroscopy. Fig. 1 shows the typical Raman spectrum of the analyzed starting GO powder. Two main peaks, first at  $1352\text{ cm}^{-1}$  and second at around  $1600\text{ cm}^{-1}$  [1]. The structures of the starting and processed material were investigated using a Philips XL30 scanning electron microscope. Fig. 2 shows the familiar micrographs of the analyzed GO powder material. X-ray diffraction and thermogravimetric analysis have also been used in the present study. For the HDDR treatment, the material being investigated was introduced in a reactor chamber and 200 mg batches were HDDR treated according to a typical cycle shown in Fig. 3.

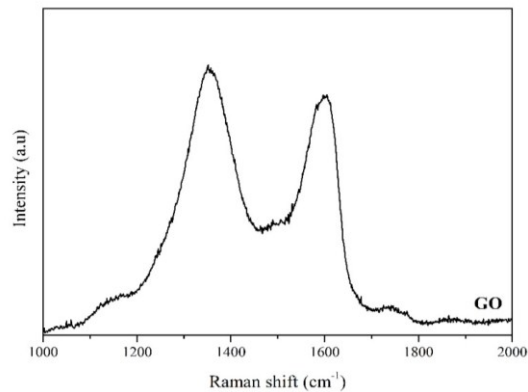


Fig. 1. Raman spectra of GO powder start material.

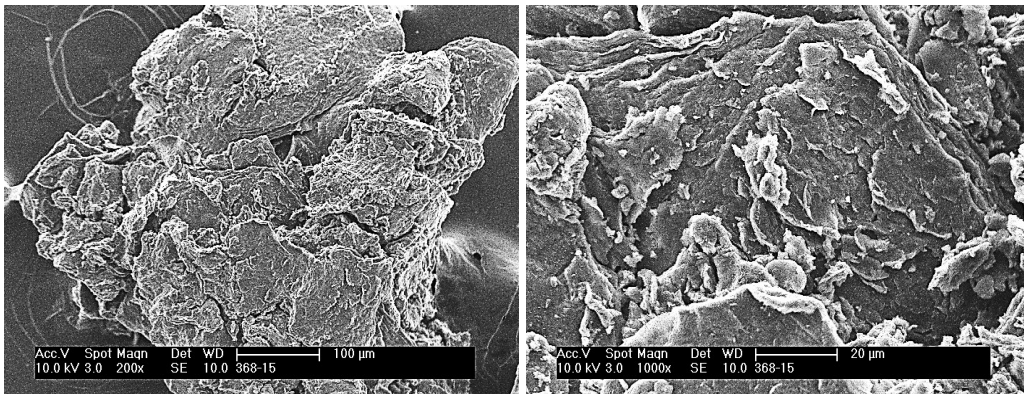


Fig. 2. SEM micrographs of GO powder start material.

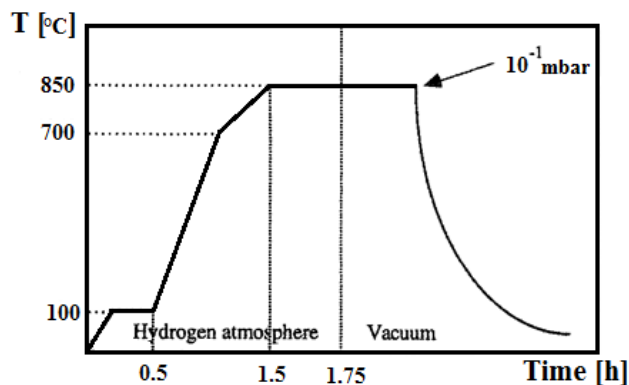
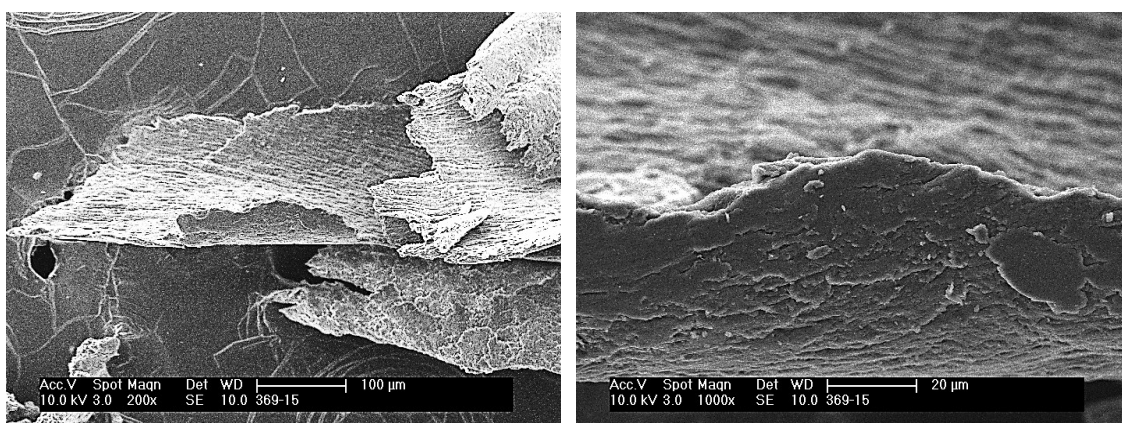


Fig. 3. Schematic diagram of the HDDR treatment cycle [9].

The supercapacitor electrodes were prepared by mixing the GO powder (or GO powder after HDDR process) with 10 wt% PTFE binder and 20 wt% carbon black conducting agent. The mixture was homogenized in isopropyl alcohol by being stirred for 30 min, and then dried for one hour at oven at 100 °C. The mixture was rolled, aiming to produce the electrodes, cut into 6 mm diameter cylinders and then pressed onto circular stainless steel substrate. The mass of active material was 13 mg. The electrical measurements were carried out at Arbin analyzer with Swagelok-type cells in standard aqueous potassium hydroxide electrolyte (6M KOH). The series equivalent resistance (ESR) was determined by discharging the fully charged supercapacitor at 1 mA F<sup>-1</sup> for 10s and reducing the current to zero. The resistance was calculated using this initial potential and the potential after 5s of null current [16]. All electrical measurements were carried out at room temperature.

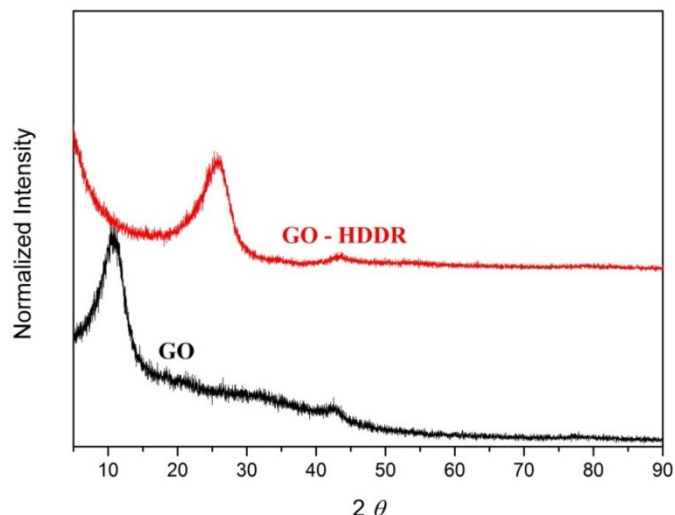
## Results and discussion

Fig. 4 shows the micrographs of the material after treatment using the standard HDDR process. Some layers of almost flat surfaces can be observed in the structure of the HDDR processed starting material. Compared to the graphene oxide microstructure (Fig.2) the features of this material are somewhat distinct showing the influence of the HDDR treatment on the GO structure.



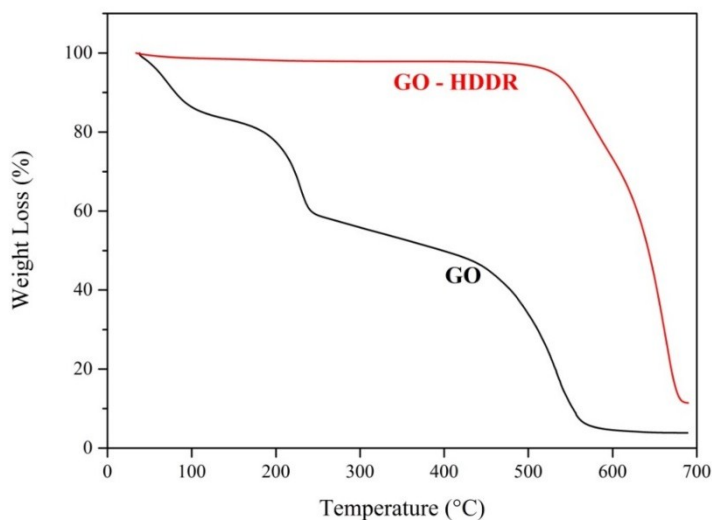
**Fig. 4.** SEM micrographs of the GO after HDDR process.

The XRD patterns of the GO starting material and after treatment using the standard HDDR process are shown in Fig.5. The GO  $2\theta$  peak at  $10.70^\circ$  showed that the starting material was in high degree of oxidation. A recent investigation on the chemical and structural analysis of graphene oxide with different degrees of oxidation has shown that with increased in the oxidation content the diffraction pattern only shows peaks due to the GO at  $2\theta = 10.91^\circ$ ,  $10.52^\circ$  and  $10.12^\circ$  [17-18]. After thermal processing under hydrogen the main peak of GO-HDDR was at  $25.81^\circ$ , showing that GO was efficiently reduced. The quality of thermally reduced GP powder increases with the decreasing of the full-width at half-maximum (FWHM) and with  $d_{002}$  approaching bulk graphite ( $2\theta = 26.7^\circ$ ) [17-18].



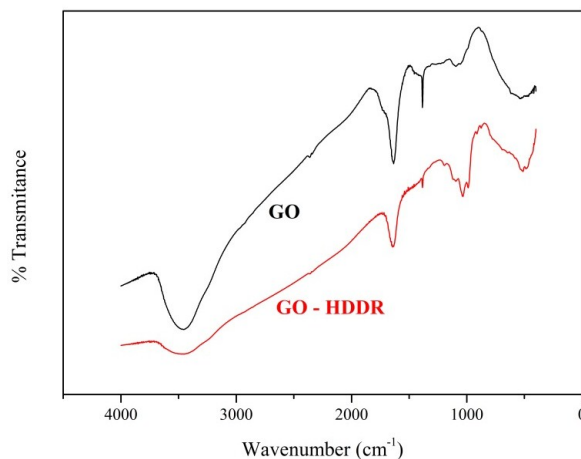
**Fig. 5.** XRD of the GO starting material and after treatment using the standard HDDR process.

Thermogravimetric analysis (TGA) plots of GO and GO after HDDR process are shown in Fig. 6. In the GO (black) sample, the major weight was lost between 100 to 300 °C, indicating water desorption from the surface at 100°C and the gradual decrease in weight from 200°C to 300°C is due to the pyrolysis of hydroxyl, epoxide, and carboxyl groups [19]. In contrast, after the HDDR process the GO (red) showed high thermal stability.



**Fig. 6.** TGA plots of GO (black) and GO after HDDR process (red).

The FTIR spectra of GO and GO after HDDR process are shown in Fig. 7. The peaks at  $\sim 3450$ ,  $\sim 1720$ ,  $\sim 1630$ ,  $\sim 1380$  and  $\sim 1220$   $\text{cm}^{-1}$  are attributed to  $-\text{OH}$ ,  $\text{C}=\text{O}$  of carboxyl groups, carbonyl,  $\text{C}-\text{OH}$  and  $\text{C}-\text{O}-\text{C}$ , respectively. As shown in Fig. 6 the peaks at  $\sim 1590$   $\text{cm}^{-1}$  were still present after the HDDR process indicating the presence of  $\text{C}=\text{C}$ , while the intensity of the absorption at  $\sim 3450$   $\text{cm}^{-1}$  (hydroxyl) and  $\sim 1380$   $\text{cm}^{-1}$  ( $\text{C}-\text{OH}$ ) decreased as a result of decomposition these groups after the HDDR process.



**Fig. 7.** FTIR spectra of GO (black) and GO after HDDR process (red).

Measured values of capacitance and ESR of the produced supercapacitors using KOH (6M) electrolyte, at room temperature, are presented in Tab. 1. It can be observed a change of both capacitance and ESR after the HDDR process. The reduction of oxygen groups showed at TGA (Fig.6) and FTIR (Fig. 7) may be explaining the decrease of equivalent series resistance of the supercapacitors. Specific capacitance increased slightly with the HDDR processing whereas ESR decreased somewhat with this procedure. The specific capacities, before and after HDDR processing, are in good agreement to those reported in Ref. [3] (189-273  $\text{Fg}^{-1}$ ). The capacitance is dependent of the maximum applied potential on measurement and organic electrolytes allow higher potential (about 2.7 V) and yield higher capacitances than aqueous electrolytes ( $\sim 1.27\text{V}$ ). The diminution on the series resistance was taken as an indicative of improvement with the HDDR processing (relative values for the present preparation condition).

**Table 1.** Capacitances and resistances per electrode of the samples supercapacitors.

Sample	Capacitance ( $\text{Fg}^{-1}$ )	ESR ( $\Omega$ )
GO	176	61
GO after HDDR	181	44

## Conclusions

Microstructural, electrical and physical changes have been produced in a graphene oxide with the HDDR process. These results showed that the HDDR process can be applied to the reduction of graphene oxide to produce supercapacitor materials. The advantage of employing this method is that the HDDR process is a relatively straightforward homogenizing and low cost treatment that might be used for large amount of material. Some improvements in the electrical properties have been obtained with this particular hydrogen thermal reduction process. Thus, the HDDR process has been considered a promising alternative method of reducing graphene oxide with efficiency and possibly in large scale production. Previously literature reported routes used a high (or ultra) vacuum system, which has a considerable capital, operational and maintenance cost for processing large quantity of materials.

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