THE PRODUCTION OF REDUCED GRAPHENE OXIDE BY A LOW-COST VACUUM SYSTEM FOR SUPERCAPACITORS APPLICATIONS

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ABSTRACT

Graphene (G) has attracted great interest for its excellent electrical properties. However, the large-scale production of graphene is still currently under investigations. Graphene oxide (GO) can be partially 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. High vacuum and temperature (10^{-7}mbar/1100ºC) is well established as an effective route for reduced powder preparation on a laboratory scale. However, a high vacuum reduction system, which can be routinely operated at 10^{-7} mbar, has a considerable capital, operational and maintenance cost to be used in a large scale. In the present

work, a low-cost route aiming large scale reduction of graphene oxide has been investigated. A stainless steel vessel has been evacuated to backing-pump pressure (10^{-2} mbar) to process graphene oxide at low and high temperatures. Attempts of reducing GO powder using low vacuum pressures have been carried out and investigated by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). The experimental results of processing graphene oxide powder at various temperatures (200-1000°C) at relatively low pressures have been reported. The microstructures of the processed material have been investigated using scanning electron microscopy (SEM) and chemical microanalyses employing energy dispersive X-ray analysis (EDX).

Keywords: Graphene Oxide, Thermal reduction, Supercapacitors, Graphene.

INTRODUCTION

Graphene oxide (GO) has been reported to have a high electrical conductivity [1]. Reduction of GO is a necessary processing step to improve the electrical conductivity for practical supercapacitors applications [2]. The reduction methods for GO material are carried out using a chemical reagent reduction or by thermal annealing although many other methods have been employed [3-5]. Recently, thermal reduction under high control atmosphere of GO have also been employed, but the cost of high vacuum pumps and gas atmosphere controller kept the price of reduced graphene oxide (rGO) extremely high. In this research, we propose a route the production of reduced graphene oxide by a low-cost under mechanical vacuum and different temperatures (200°C to 1000°C).

EXPERIMENTAL

Graphene oxide was prepared using a modified Hummers' method [6]. Graphite powder, $NaNO_3$ and H_2SO_4 were briefly stirred in an ice bath. $KMnO_4$ was then gradually added and the temperature was kept at about 35°C for one hour. Subsequently, deionized (DI) water was added followed by H_2O_2 (30%)

turning the color of the solution from dark brown to yellow. The product was washed with DI water, NaOH (1M) and HCl (1M) until pH 7. All the work up steps was 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. The structures and chemical composition of the starting material were investigated using a Philips XL30 scanning electron microscope (MEV) and X-ray fluorescence (XRF).

For the reduction of graphene oxide, the material being investigated was introduced in a reactor chamber and 200 mg batches. Then the mechanical vacuum has been started until the chamber pressure reduces to 10^{-2} mbar. After the chamber was heat under vacuum. The temperatures starting in 200°C until 1000°C was selected to investigate the thermal reduction of graphene oxide.

The X-ray diffraction powder (XDR) and Fourier transform infrared spectroscopy (FTIR) have also been used to investigated the reduction of graphene oxide in the present study.

RESULTS AND DISCUSSION

Fig. 1 shows the familiar micrographs of the analyzed GO powder material obtained from modified Hummers' method.

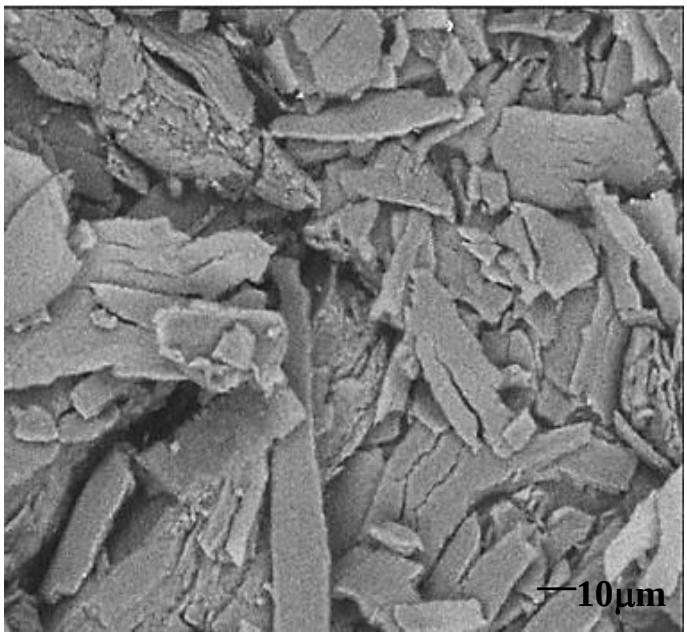

Figure 1. SEM micrographs of GO powder start material obtained from modified Hummers' method.

Fig. 2 shows the X-ray fluorescence of the GO powder material obtained from modified Hummers' method.

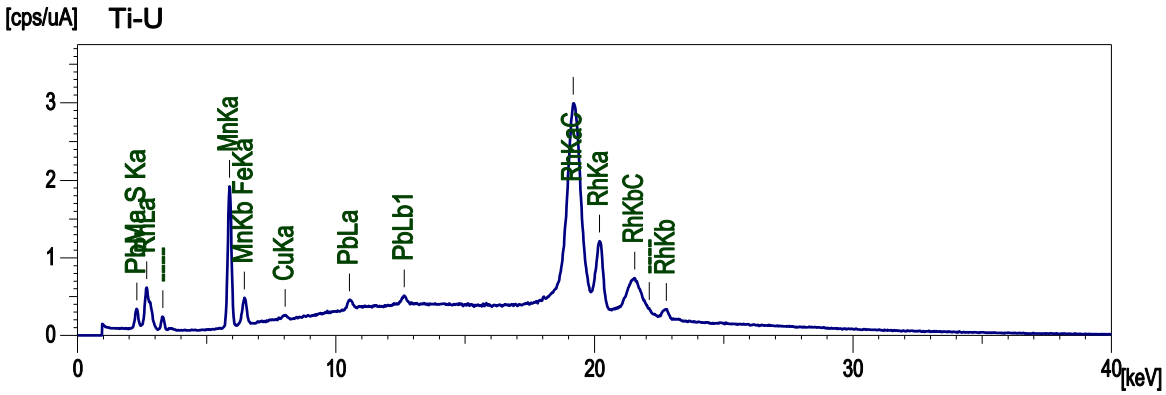

Figure 2. XRF energy spectrum of GO powder start material obtained from modified Hummers' method.

The FTIR spectra of GO after thermal reduction process at different temperatures are shown in Fig. 4. It clear observed a considerable an intensity of variation of bands with increasing processing temperature. Graphene oxide spectrum processed under vacuum at 200° C shows a well-defined band between 1500 and 2000 cm^{-1}. This band disappears in turn processing temperatures higher than 200°C. On the other hand, at 800°C the band between 3700 and 3000 cm^{-1} changed substantially pronounced in graphene oxide processed.

At 200°C, it is possible to verify a presence of a spectral band ranging from 3417 cm^{-1}, allowing an association to this nitrogen region (CH, OH and NH), giving then an essential feature for the presence of reduced graphene oxide. At the wavelength of 1730 cm^{-1} region carbonyls can be seen from carboxylic acids.

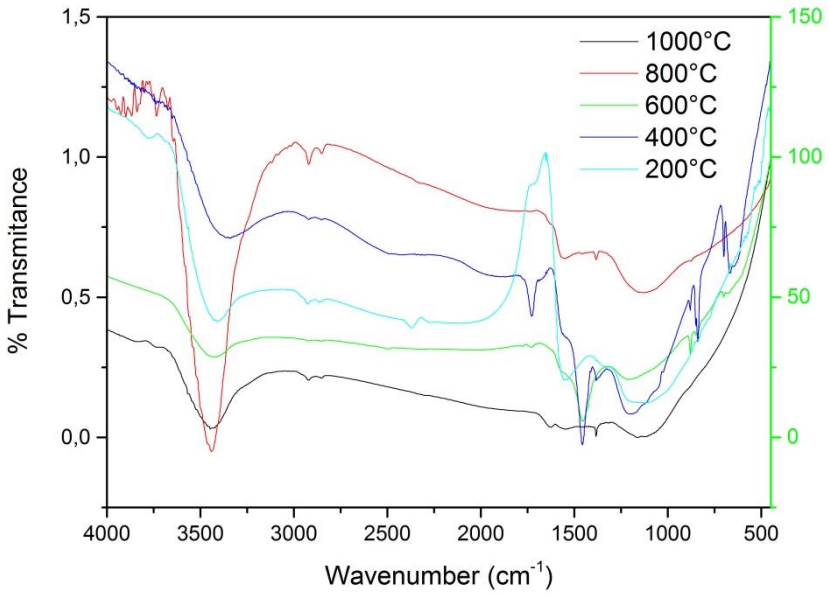

Figure 4. FTIR spectra of the GO after thermal reduction process to 200°C until 1000°C.

The XRD patterns of the GO starting material and after thermal reduction temperatures are shown in Fig.5. Two peaks can be observed, the first, most intense in 2θ = 10,81º and the second, less intense in 2θ = 42,59º. The position changing of the first peak can be observed with the processing of GO under vacuum. The position of peaks at different thermal process are listed in Tab. 1.

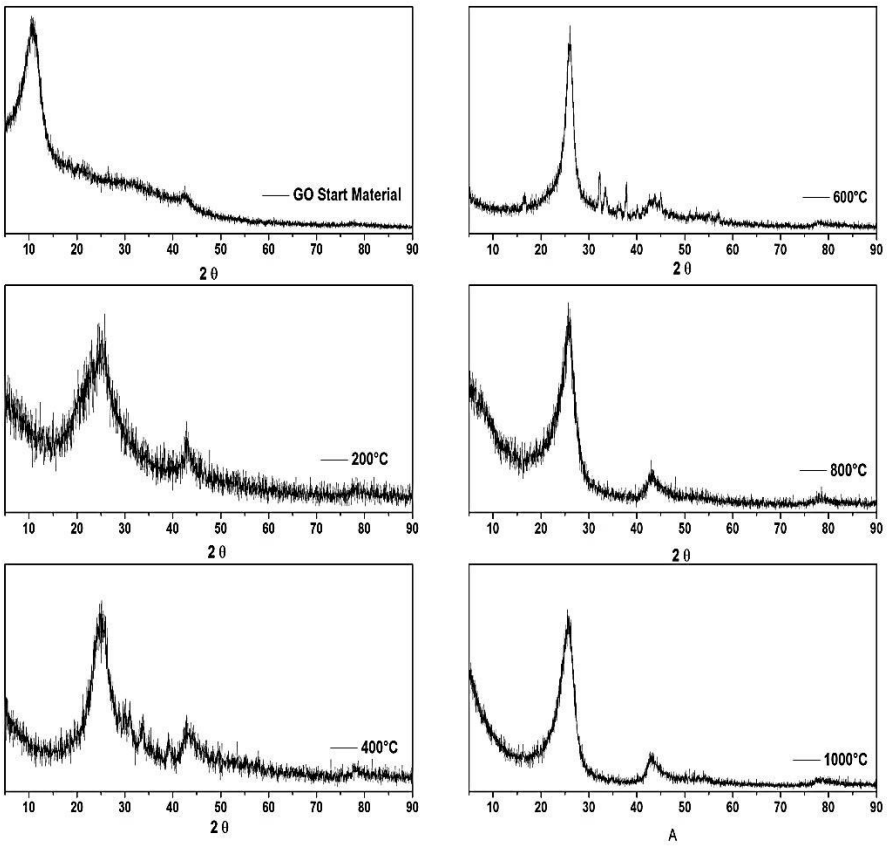

Figure 5. XRD of the GO starting material and after thermal treatment process at different temperatures.

Table 1. Peak position in different thermal reduction of GO.

Temperatura (°C)	Crystallographic Plane	
	(002)	(100)
GO start material	10,81	42,59
200	25,73	42,77
400	25,01	42,89
600	25,96	43,48
800	25,84	43,00
1000	25,49	42,89

Based on the analysis performed in this paper could be concluded that the GO reduction process in a vacuum produced with mechanical pump was possible from 200 ° C. This considerably increases the economic viability of industrial-scale to production of the reduced graphene oxide (rGO) using relatively small and inexpensive vacuum system with dual-stage mechanical pump temperatures (≥10-3 mbar).

CONCLUSION

This paper has shown that influence of temperature in a thermal reduction of graphene oxide. The intensity of bands changing at FTIR analysis may be observed with increase of temperature in a thermal reduction. A well-defined band between 1500 and 2000 cm^{-1} shown only at 200°C temperature. Distinctly, a band between 3700 and 3000 cm^{-1} became substantially only pronounced in graphene oxide sample processed in vacuum at 800 ° C. Two at XRD analysis were obtained with GO produced by Hummer's method. The first and most intense in 2θ = 10,81º and the second lower intensity in 2θ = 42,59º. This thermal process under vacuum shifted the first peak to $2\theta \approx$ 25º. It could be conclusion of the reduction of GO.

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