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The Production of Reduced Graphene Oxide by a Low-Cost Vacuum System for Supercapacitor Applications

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Abstract. Graphene has attracted significant interest because of its excellent electrical properties. However, a practical method for producing graphene on a large scale is yet to be developed. Graphene oxide (GO) can be partially reduced to graphene-like sheets by removing the oxygen-containing groups and recovering the conjugated structure. GO can be produced using inexpensive graphite as the raw material via cost-effective chemical methods. High vacuum and temperature (10^{-7} mbar and 1100°C, respectively) conditions are well-known to enable the preparation of reduced powder at the laboratory scale. However, a large-scale high vacuum reduction system that can be routinely operated at 10^{-7} mbar requires considerable initial capital as well as substantial operational and maintenance costs. The current study aims at developing an inexpensive method for the large-scale reduction of graphene oxide. A stainless steel vessel was evacuated to backing-pump pressure (10^{-2} mbar) and used to process GO at a range of temperatures. The reduction of GO powder at low vacuum pressures was attempted and investigated by X-ray diffraction and Fourier transform infrared spectroscopy. The experimental results of processing GO powder at various temperatures (200–1000°C) at relatively low pressures are reported. The microstructures of the processed materials were investigated using scanning electron microscopy and chemical microanalyses via energy dispersive X-ray analysis.

Introduction

Graphene oxide (GO) has been reported to have a high electrical conductivity [1]. However, GO must be reduced in order to improve the electrical conductivity for practical supercapacitor applications [2]. GO materials are typically reduced using a chemical reagent or by thermal annealing, although many other methods have been employed [3-5]. Recently, thermal reduction of GO under a highly controlled atmosphere was reported; however, the cost of the high vacuum pumps and gas atmosphere controller results in an extremely high price for reduced graphene oxide (rGO). In this research, we propose an inexpensive route for the production of rGO under a mechanical vacuum at a variety of temperatures (200–1000°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. The addition of deionized (DI) water followed by H_2O_2 (30%) generated a change in the color of the solution from dark brown to yellow. The product

was washed with DI water, NaOH (1 M), and HCl (1 M) until the solution reached pH 7. The sample was then centrifuged at 12000 rpm for 10 min. The resultant GO samples were dispersed in ethanol, exfoliated using ultrasonication, and then dried for further analysis. The structures and chemical compositions of the starting material were investigated using scanning electron microscopy (SEM; Philips XL30) and X-ray fluorescence (XRF).

To reduce graphene oxide, the GO material was placed in a reactor chamber in 200 mg batches. The pressure of the chamber was reduced to 10^{-2} mbar using a mechanical pump, and the chamber was then heated. The temperatures investigated ranged from 200 to 1000°C in order to elucidate the thermal reduction of graphene oxide.

X-Ray powder diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) were also used to characterize the reduction of GO.

Results and Discussion

Fig. 1 shows a typical micrograph of GO powder material obtained using the modified Hummers' method.

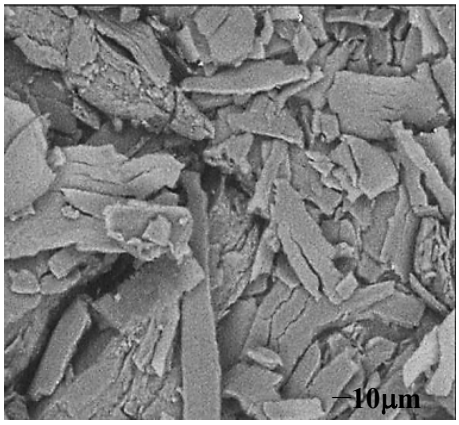

Fig. 1. SEM micrograph of the GO powder starting material obtained using the modified Hummers' method.

Fig. 2 shows the XRF energy spectrum of the GO powder material obtained using the modified Hummers' method.

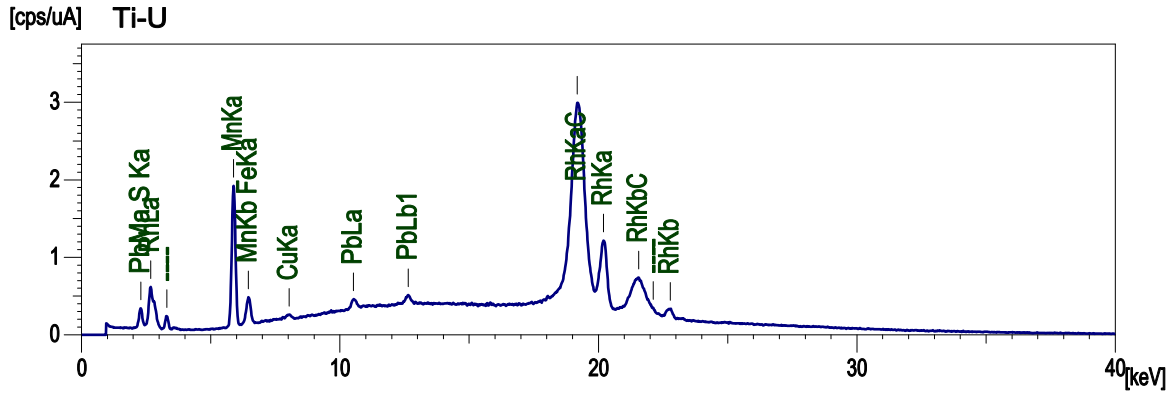

Fig. 2. XRF energy spectrum of the GO powder starting material obtained using the modified Hummers' method.

The FTIR spectra of GO after thermal reduction at different temperatures are shown in Fig. 3. The spectra show considerable variation in the intensities of the bands with varying processing temperatures. The spectrum of GO processed under vacuum at 200°C shows a well-defined band between 1500 and 2000 cm^{-1}; this band disappears at processing temperatures greater than 200°C. However, after processing GO at 800°C, the band between 3000 and 3700 cm^{-1} becomes significantly more pronounced.

At 200°C, it is possible to identify a spectral band centered at 3417 cm^{-1}; this is associated with CH, OH, and NH moieties, which are essential indicators of rGO. In addition, the carbonyl moieties of the carboxylic acid groups are evident at 1730 cm^{-1}.

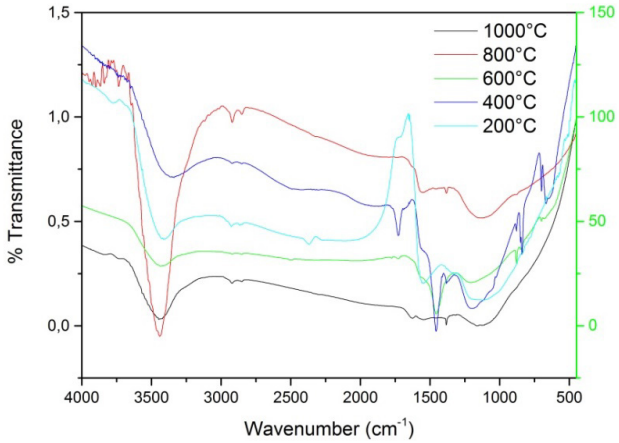

Fig. 3. FTIR spectra of the GO after thermal reduction at various temperatures (200–1000°C).

XRD patterns of the GO starting material before and after thermal reduction at various temperatures are shown in Fig. 4. Two peaks are evident in the patterns: The first peak appears at 2θ = 10.81° for GO, and the second peak, which is less intense, appears at 2θ = 42.59° for GO. After processing GO under vacuum, the position of the first peak undergoes a shift; the magnitude of this shift is dependent on the processing temperature. The positions of the peaks for GO processed at different temperatures are listed in Table 1.

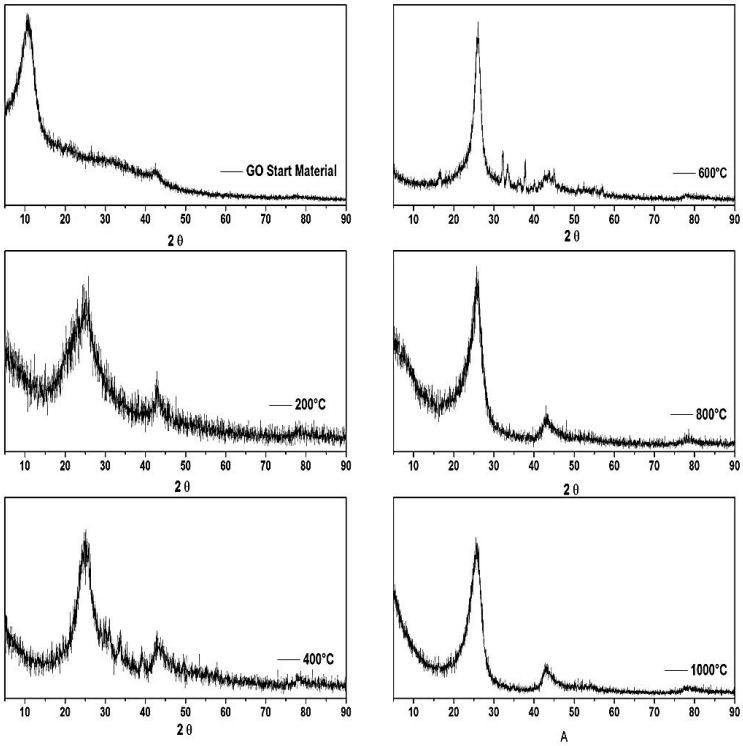

Fig. 4. XRD patterns of the GO starting material before and after thermal treatment at different temperatures.

Table 1. Peak positions in the XRD patterns of GO reduced at different temperatures.

Temperature (°C)	Crystallographic Plane	
	(002)	(100)
GO starting 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, we concluded that GO could be reduced under a vacuum produced using a mechanical pump at temperatures as low as 200°C. These results considerably increase the economic viability of industrial-scale production of rGO using a relatively small and inexpensive vacuum system with dual-stage mechanical pump pressures (≥10–3 mbar).

Conclusion

This study elucidated the effect of temperature on the thermal reduction of GO. The intensities of the bands in the FTIR spectra were affected by the temperature used for thermal reduction. A well-defined band between 1500 and 2000 cm^{-1} was only present when the reduction occurred at 200°C. A distinct band between 3700 and 3000 cm^{-1} became substantially more pronounced in the spectrum of the GO processed under vacuum at 800°C. Two peaks were evident in the XRD pattern of the GO produced using a modified Hummer's method: The first peak occurred at $2\theta = 10.81°$, and the second peak, which was of lower intensity, appeared at $2\theta = 42.59°$. After thermal processing under vacuum, the first peak shifted to $2\theta \approx 25°$, which confirms the reduction of GO.

Acknowledgements

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