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Plasma-Based Graphene Functionalization in Glow Discharge

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Abstract

Glow discharge was utilized to add oxygen functional groups to the graphene platelets sample produced in chemical exfoliation synthesis. It was concluded based on Raman spectra that the graphene sample treated with the glow discharge preserves specific graphene features while no transformation to amorphous carbon is happening. SEM and EDS results indicated the increases of oxygen content in the graphene sample after the exposure to the glow discharge. Raman spectra also support the fact that the graphene platelets have been decorated with oxygen as the result of the glow discharge treatment.

Keywords

Graphene, Functionalization, Plasma-Based

1. Introduction

Graphene is a flat, atomic-scale, honeycomb lattice [1], which is made of carbon atoms with a flat hexagonal atomic structure [2]. It is the world's first 2D material which extends only in length and width. This gives graphene a set of unique properties which has caught a lot of researcher's attentions [3]. It can dramatically improve the thermal and electrical conductivity of the medium it is added to, and significantly increases strength [4]. However, graphene is inherently inert and it does not always bond properly with the matrix on its own. Instead, graphene flakes tend to agglomerate resulting in its non-uniform distribution in final composite. In order to prevent this, functional groups must be added to the graphene [5] [6]. Other applications requiring graphene functionalization include membrane seperation and dehydration of organic or water mixture [7]-[9], etc. Ultra thin Graphene oxide membrane separation realizes high-flux, high-sensitivity mixture separation at low energy cost. Pristine multi-layered graphene oxide coated onto a thin film nano-fibrous composite (TFNC) mat forms a high flux membrane for organic or water dehydration. This is because once oxygen is added, there will be

breaking of C-C bonds and releasing of C atoms, introducing defects; and oxygen groups can swell the interlayer-spacing.

There are several methods to functionalize graphene and the most widely utilized is chemical functionalization [11]. This method is accompanied with numbers of disadvantages such as utilization and production of non-environmental friendly chemicals as well as adding an extra step to the synthesis process [12]. Another approach is to use plasma-based functionalization [13], which is benefited by increasing reactivity of the species. In addition, plasma-based functionalization enables functionalization as part of the synthesis process and it is also environmentally friendly. Different types of discharges such as microwave-excited surface-wave plasma [14], DC, RF plasmas were used to functionalize nanostructures [15]. SWCNTs were successfully functionalized with F, NH [16] [17], etc. In addition, the advantages of the plasma-based functionalization compared to wet chemical reactions were concluded. Other methods of graphene functionalization include ultraviolet oxidative treatment [18], ozone treatment [19]-[21], and photochemical oxidation [22].

However, there was no significant research done on plasma-based graphene functionalization. This work is focused on studying the benefits of glow discharge utilization for decorating graphene with oxygen functional groups (see **Figure 1**).

2. Experimental Setup and Procedure

The experiment was conducted inside a stainless steel chamber (45 cm in diameter and 64 cm in length) pumped with mechanical pump to the residual air pressure of about 10^{-1} torr. A piece of copper wire with the diameter of 0.3 mm was used as the substrate and a little pitch of graphene flakes prepared by chemical exfoliation method (N006-P Polar Graphene Powder by Angstron Materials Inc) was placed on the substrate. Adjustable AC voltage up to ~550 V was applied to the copper substrate with respect to chamber walls as shown schematically in **Figure 2**.
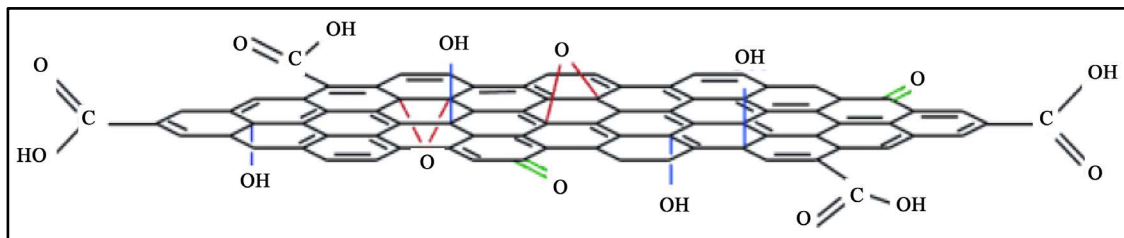

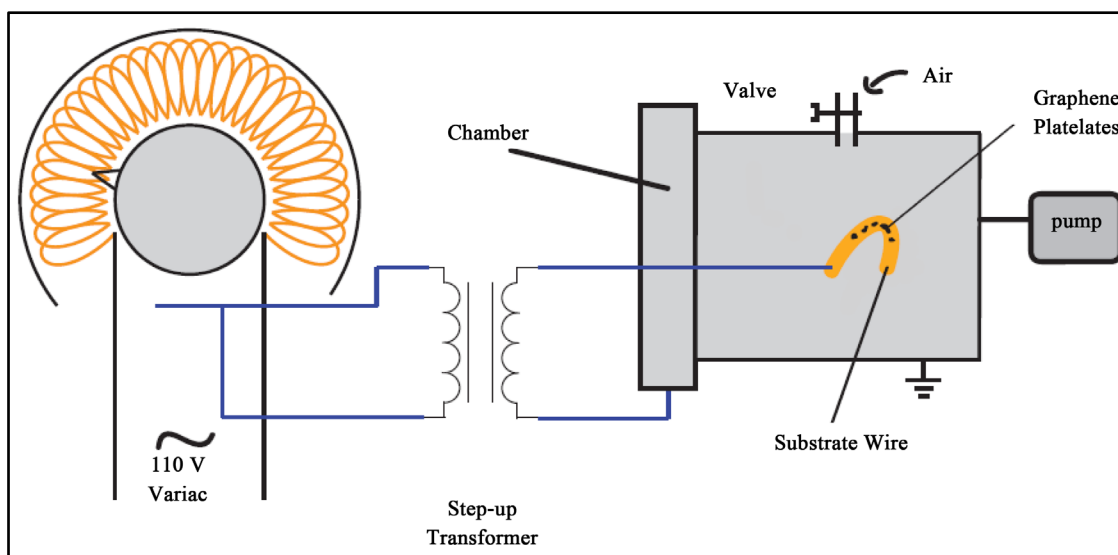**Figure 1.** Graphene functionalized with O and OH groups [10].

Figure 2. Experimental setup.

The glow discharge of alternative current was ignited when amplitude of the applied AC voltage exceeds U ~ 320 V [23]. The experiments were conducted at U ~ 476 V and exposure time was 90 s. The glow discharge was concentrated around the substrate with graphene as shown in **Figure 3**.

The samples were characterized of using SIGMA VP-02-44 SEM equipped with OXFORD INCA x-act ADD0048 EDS and Horiba LabRAM Raman HR 800 spectrometer. Five randomly chosen points on the each sample were observed for averaging.

3. Results and Discussions

SEM images of treated and untreated samples are shown in **Figure 4**. No changes of morphology in the samples after the treatment were found. EDS results are shown in **Table 1**. It was observed that the average oxygen weight content (averaged over 5 randomly chosen points) was 2.31% before the exposure. After exposure to the glow discharge, the oxygen percentage rose to 4.74% which is an increase by 105.2%. The admixture of copper in the samples was found to be less than 1%.

As a next step it was determined using Raman Spectrometer whether flakes treated in plasma are still graphene, as opposed to amorphous carbon. This characterization procedure was performed with a Horiba RAMAN spectrum at room temperature. **Figures 5(a)-(c)** show Raman spectra of untreated and treated graphene sample. Three intense features D, G, G' peaks could be observed along the spectra at around 1355 cm^{-1}, 1575 cm^{-1} and 2700 cm^{-1}. The D peak is associated with the amount of defects in sp2 bonds [24] and G peak is related to doubly degenerate E2g mode [25]-[27]. G' peak has nothing to do with G peak while its shape could be used to determine the number of layers of the graphene flakes. It can be seen the spectra for both treated and untreated flakes
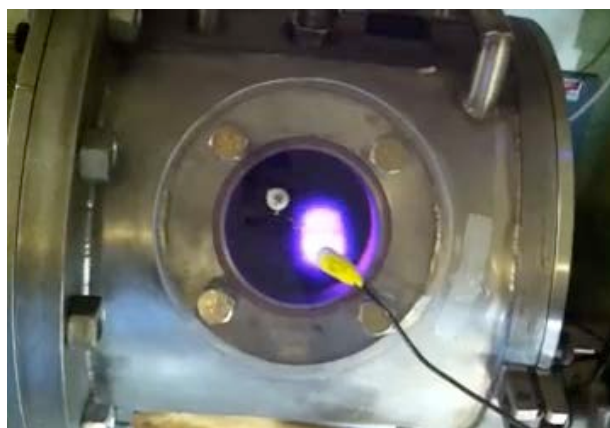

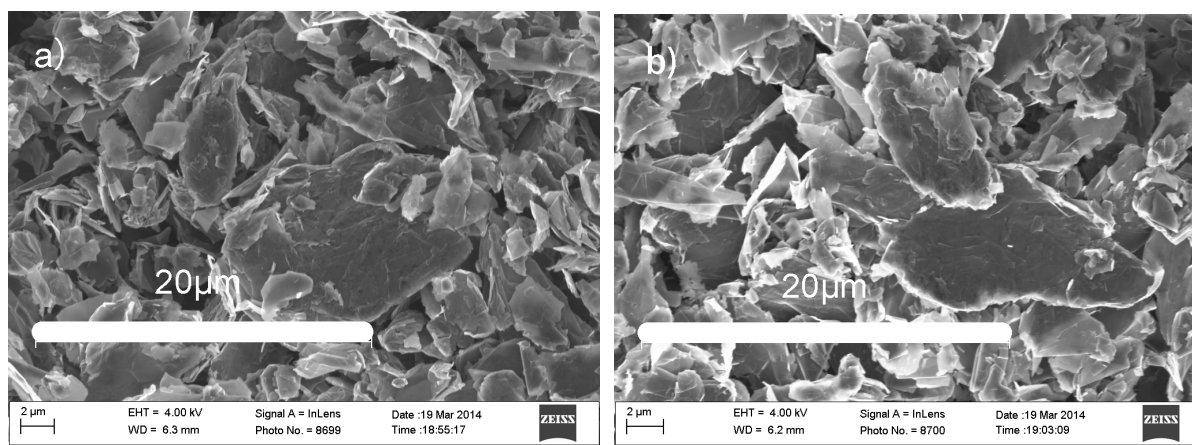**Figure 3.** Glow discharge generated between two electrodes.

Figure 4. SEM images of N006-P Polar Graphene Powder which were observed under EDS (a) before and (b) after the exposure to the glow discharge.
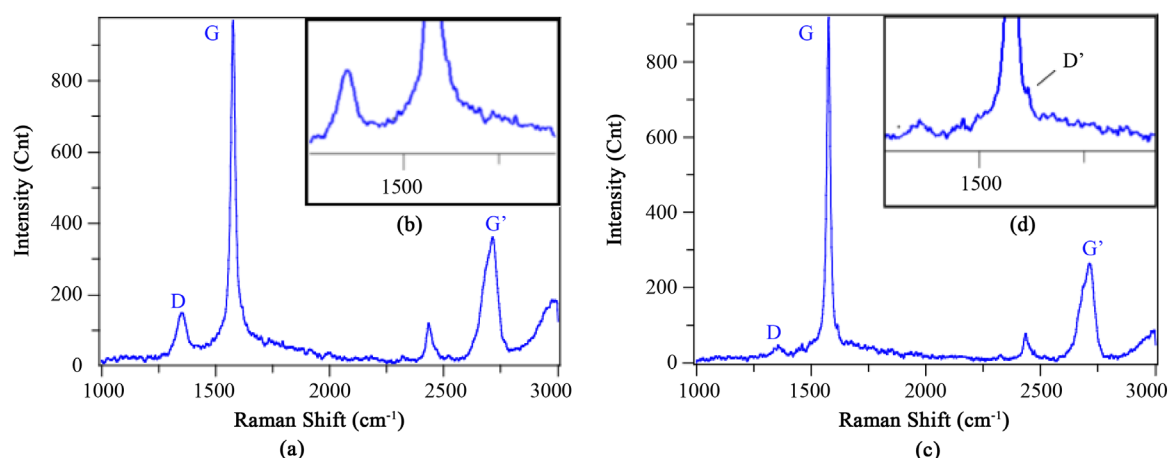
Figure 5. RAMAN spectra of (a)-(b) untreated N006-P Polar Graphene Powder and (c)-(d) plasma-treated N006-P Polar Graphene Powder.

Table 1. EDS material weight percentage of carbon and oxygen before and after exposure to the glow discharge.

Weight%	Element	Point 1	Point 2	Point 3	Point 4	Point 5
Before Exposure	Carbon	97.82%	97.36%	97.16%	97.80%	98.31%
	Oxygen	2.18%	2.64%	2.84%	2.20%	1.69%
After Exposure	Carbon	94.50%	93.63%	96.82%	96.14%	95.21%
	Oxygen	5.50%	6.37%	3.18%	3.86%	4.79%

were similar, and the ratio of I(G')/I(G) still remains 0.5.

The main difference on the Raman spectra was presence of small D' peak on the plasma treated sample as shown on the zoomed to the range 1250 - 1700 cm^{-1} spectra shown in **Figure 5(d)**. After the employment of the glow discharge, one can see that averaging of many RAMAN spectra indicate presence of small D' peak on treated sample. Presence of D' is indicator of graphene oxide according to Baraket *et al*. [28].

From the results above, one could tell there is a significant increase of oxygen content after the exposure to the glow discharge, while the graphene flake structure did not undergo significant change. After determining the elemental makeup of the graphene structure.

Future experiments will have to address influence of exposure duration and discharge voltage on the efficiency of functionalization and extend characterization of the functionalized graphene (e.g. XPS, XRD, AFM etc.).

4. Summary

We have shown that plasma-based glow discharge technique can be used for oxygen functionalization of graphene platelets. It is important to point out that the graphene sample did not changed into amorphous carbon after the exposure. SEM, EDS and Raman diagnostics inform about effective oxygen functionalization. Oxygen content was increased by factor of 2 after plasma exposure of 90 seconds. In addition, Raman spectra show presence of small D' peak, which also indicates elevated presence of oxygen in the plasma treated sample. More detailed investigation of treatment conditions (voltage, time) is required in future in order to improve controllability of the glow discharge graphene modification.

Acknowledgements

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