Synthesis of Reduced Graphene Oxide Films using Atmospheric Plasma Annealing

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ABSTRACT

Samples of nickel foam soaked with graphene oxide were subjected to atmospheric plasma annealing (APA) using nitrogen as the ionizing gas. The processed samples were then characterized using ESEM, XPS and FTIR. The results from the samples subjected to APA indicate that it is possible to synthesize reduced graphene oxide by this technique.

Key Words: Atmospheric Plasma Annealing, reduced graphene oxide, XPS, ESEM, FTIR

INTRODUCTION

The synthesis of reduced graphene oxide (RGO) has been accomplished by various methods including chemical reduction [1,2], annealing GO in hydrogen plasma [3,4] exposing GO to laser light in a light scribe [5], and directly heating GO to a temperature of 700°C in a furnace [6]. The reduction of GO to RGO enhances the conductivity of the film and makes it attractive as an electrode for supercapacitors [7]. However, the interaction of pi electrons between graphene sheets reduces the capacitance of these graphene-based supercapacitors [8]. Ni foam soaked with GO has been reported to have better properties than common electrodes, which have expensive metals such as gold and platinum mixed with binder applied on the anode [8]. The fabrication of a nickel foam-supported electrode that is GO-based could eliminate the need for a binder and significantly reduce the cost of the electrode.

In this paper we present the results of an investigation to synthesize RGO using a fast, safe, and nontoxic method. Atmospheric Plasma Annealing (APA) generates compressed-air cold plasma, using various ionized gases. When GO-soaked nickel foam is subjected to APA using nitrogen plasma, the oxygen from the GO is removed by the nitrogen from the plasma and RGO is found to result. This technique enables rapid reduction of GO without the use of hydrogen gas, thereby making the process safer. The presence of RGO after APA was identified using analysis of data obtained from environmental scanning electron microscopy (ESEM), X-ray photoemission spectroscopy (XPS) and Fourier Transform Infrared Spectroscopy (FTIR).

METHODS

Sample Preparation

Commercial grade graphene oxide (4mg/ml concentration) was purchased from Sigma Aldrich. Nickel foam was purchased from Novamet and 1-inch diameter foam disks were punched out. The samples were prepared by soaking the nickel foam disks in the GO solution with sonication for 30 minutes, and then allowed to dry at room temperature. Upon drying, the graphene oxide loading on the disks was approximately 0.1g each. The samples were annealed using APA, a scanning, DC-pulsed plasma system supplied by PlasmaTreat. Nitrogen was used as the ionizing gas. The number of plasma scans were varied from 10-18. The diameter of the plasma jet was 0.5cm. The temperature of the backside of the foam (the face opposite the incoming plasma jet) was found to range from 180°C to 280°C when the plasma nozzle was maintained at a distance of 1cm from the sample surface.

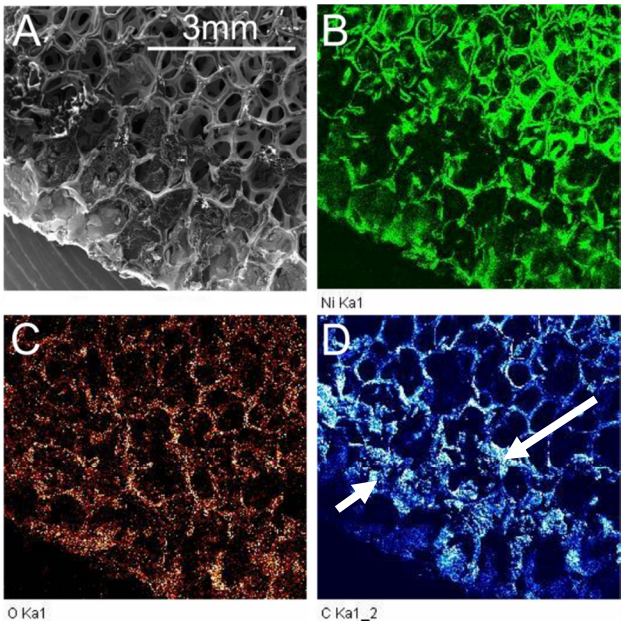

Figure 1: A) ESEM image after 12 scans of APA. B), C), D) display chemical maps shown by brightness of nickel, oxygen, and carbon respectively. Arrows indicate carbon-rich regions.

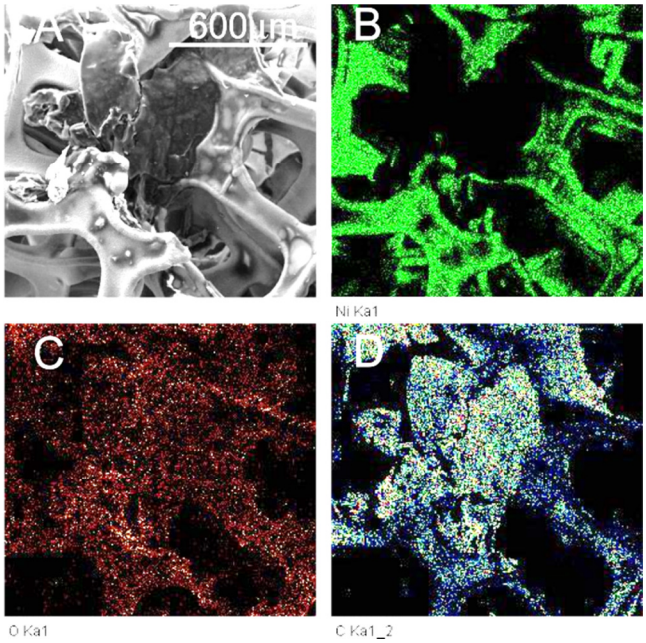

Figure 2: A) ESEM image after 18 scans of APA. B), C), D) display chemical maps shown by brightness of nickel, oxygen, and carbon respectively.

Sample Characterization

Three different techniques were used to characterize the samples after APA treatment. ESEM data was obtained using a Quanta 200s Environmental Scanning Electron Microscope (ESEM) system. In addition to images of the sample surfaces, this device can provide the chemical composition of the samples over a specified area to a depth of a few micrometers. The ratio of carbon to oxygen was calculated at different locations on a sample and the average value of at least 3 locations was obtained. Chemical mapping was performed on two samples, one with 12 scans and another with 18 scans, to determine if the oxygen was found on the carbon-rich areas or on the exposed nickel-foam areas. A Physical PHI Electronic-X Tool Model XPS was used to determine if the carbon found after annealing had significant binding energies characteristic of SP^2 hybridized carbon or if carbon-oxygen bonds were prevalent. ATR-FTIR analysis was performed using a Nicolet 50 infrared spectrometer. An analysis of the spectra determined if there was reduction in the O-H bonds and C-O bonds, to indicate a decrease in oxygen content.

RESULTS

Chemical composition maps of annealed Ni Foam/GO samples obtained from ESEM suggest that there may be an optimal range of APA passes for successful RGO production. Figure 1A displays an ESEM image of a sample of Ni foam soaked with GO after 12 APA scans. The image shows a characteristic graphene oxide film on the nickel foam, and carbon-rich areas have formed on the surfaces of the sample. Arrows indicate the carbon rich areas on the map (Figure 1D). However, similar data from a sample processed with

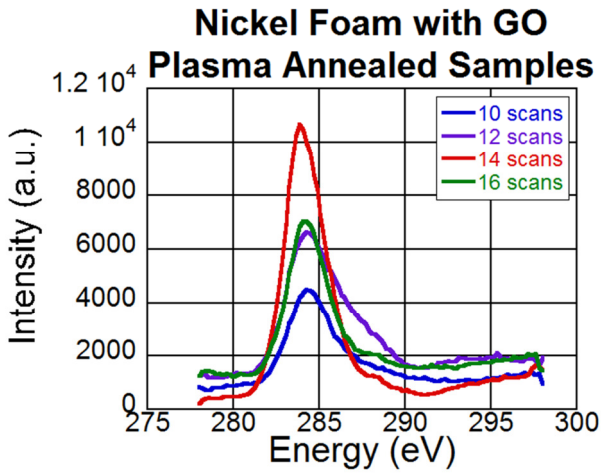

Figure 3: XPS data displaying binding energies of carbon from nickel foam soaked graphene oxide subjected to varying number of plasma scans.

18 plasma scans (Figures 2A, B, C and D) exhibited a greater correlation between regions rich in both oxygen and carbon, suggesting that more oxygen was bound to carbon than in Figure 1. The data suggests that there could be an optimum temperature within the measured range of temperatures (180°C to 280°C for 10 to 18 scans respectively) for the formation of RGO on a nickel foam support.

ESEM chemical composition measurements were used to calculate the atomic percentage of carbon and oxygen at different regions on sample surfaces. Table 1 reports the average ratio of carbon to oxygen obtained from samples subjected to a APA scans ranging from 10-18. The averages were calculated over regions varying in area from tens to hundreds of micrometers. The ratio of carbon to oxygen suggests there might be a threshold number of APA scans to reduce GO to RGO. The higher C:O ratio with increase in APA scans might suggest that Ni foam/GO samples yield more RGO; however, as shown in Figure 1, the oxygen observed in samples annealed with 12 APA scans appears to be bound to the nickel foam, and not to the carbon on the sample's surface. Despite the elevated ratio of carbon to oxygen with increased number of APA scans, it appears that there an intermediate number of scans yields greater RGO production than 18 APA scans. The ratio of carbon to oxygen alone does not seem to be a reliable indicator of RGO production on nickel foam. Additional experiments are underway to investigate this further.

# Scans	Average C:O
0	2
10	0.9
12	10.4
16	9
18	13.9

Table 1. Ratio of carbon to oxygen as calculated from ESEM chemical composition measurements. Increasing number of scans of APA during annealing correlates with an increased ratio of carbon to oxygen in resultant samples.

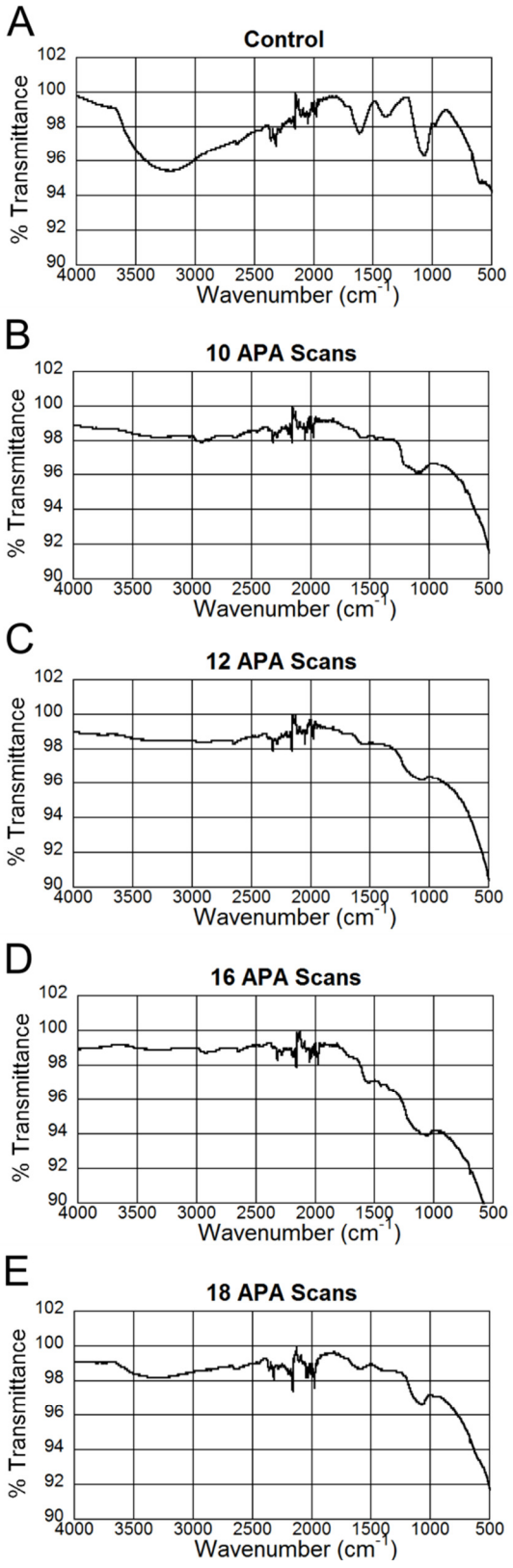

Figure 4: Percent transmittance as measured by FTIR for Nickel Foam soaked in graphene oxide A) without annealing, and after B) 10 APA scans, C) 12 APA scans, D) 16 APA scans, and E) 18 APA scans in nitrogen gas.

To further investigate whether APA-based annealing removed carbon-oxygen bonds and enhanced carbon-carbon bonds (typical in RGO vs GO) we used XPS to investigate the surface chemistry of our samples. Figure 3 displays XPS data from the samples annealed with 10, 12, 14 and 16 scans. A binding energy of 284.5eV is characteristic of C=C (SP^2) bonds [1]. Our data presents significant intensity centered on that value and lower intensities at higher binding energies characteristic of carbon-oxygen bonds. This result will be more obvious after data fitting is done. Although some C-O and C=O bonds (~286eV and 289eV) are present after 10 and 12 scans, they are considerably lower in intensity than the feature at 284.5eV. The intensity of the spectral signature at 284.5eV is found to grow when the number of scans increases from 10 to 12 and we observe that this feature diminishes for APA of 16 or more scans, further supporting the evidence from ESEM measurements that indicate an ideal intermediate annealing time/temperature.

Fourier transform infrared spectroscopy was also used to investigate the surface chemistry of our samples. FTIR spectra from samples that were annealed for 0 (unannealed), 10, 16, and 18 scans of APA in nitrogen gas are displayed in Figure 4. The characteristic absorption due to O-H bonds at 3340cm^{-1} and the C-O bond at 1067cm^{-1} are prominent in the control sample, which underwent no annealing. Upon APA with 10 or more scans, both these features are substantially reduced. The sample subjected to 18 scans showed more OH absorption than the one subjected to 10 scans supporting the evidence provided by ESEM and XPS measurements that there is an intermediate number of scans that results in optimal reduction of GO on nickel foam.

CONCLUSIONS

RGO can be formed by subjecting nickel foam soaked with GO to APA using nitrogen ions. An analysis of the data using ESEM, XPS, and FTIR while increasing the number of nitrogen plasma scans from 10 to 18 indicates that there may be an intermediate number of scans that results in optimal reduction of GO. Although the substrate temperature of nickel foam was low at 180-280^{o}C, it is possible that the surface of the sample attained a higher temperature. Researchers at Stanford have reported that N-doping can occur at temperatures of about 300^{o}C [9]. In addition, they report a better reduction of oxygen when their samples were subsequently annealed with ammonia plasma. We believe the nitrogen ion plasma applied to graphene oxide in air could have caused temporary nitrogen doping. No nitrogen signature was observed in the XPS data collected after annealing. The doping of nitrogen from the atmosphere in GO could have enhanced the reduction process and caused the formation of RGO when nitrogen plasma was applied. Ultimately, using the method described here, the complete reduction of graphene oxide is limited since these films are annealed in atmosphere and exposed to air during the treatment. Shrouding the plasma jet to reduce the oxygen content in the area surrounding the substrate may improve the degree of reduction for the graphene oxide films.

Additionally, by purely exposing the substrates to the plasma for specific time intervals as opposed to scanning may increase exposure to the radicals produced by plasma and may improve the degree of reduction. Further experiments are necessary to investigate this.

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