Effect of PVA Addition on SO$_2$ Adsorption Properties of GO Fibers

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Abstract Since late 20th century, the drawbacks of pollution became obvious which increases the demand for environmental friendly and ecological approaches in all disciplines. Not only using environment friendly materials and procedures, but also detecting any pollution, and potential solutions are also common area of current research. SO$_2$, one of the significant topics in waste management, is reported to cause acidic rain. To abolish SO$_2$ waste, excess temperature is required. The current efforts are to develop materials that can remove SO$_2$ at comparatively low temperatures. The aim of this study is to examine a potential use of graphene oxide (GO) fibers and composite polyvinyl alcohol (PVA) incorporated GO fibers in SO$_2$ filters. So as to observe the effect of PVA incorporation on composite fiber properties, PVA incorporated GO fibers and neat GO fibers were prepared. GO fibers were prepared with modified Hummers method followed by wet spinning through three coagulation baths. For composite fiber formation, 10% PVA was added to coagulation bath three. So formed fiber morphologies were analyzed with SEM, AFM and BET. Electrical conductivities were calculated from electrical resistances measured with conductivity tester. The SO$_2$ adsorption and desorption properties were measured in a quartz reactor. PVA addition did not have a significant effect on electrical conductivity whereas increases the SO$_2$ adsorption capacity and reduces the surface roughness, pore size, pore volume and surface area.

Keywords—graphene oxide, SO$_2$ adsorption, electrical conductivity, PVA.

1. INTRODUCTION

SO$_2$, an industrial and exhaust waste, is one of the major pollutants causing environmental damage. Increase in SO$_2$ level rises the greenhouse effect and results with acidic rain. Current efforts are to develop gas sensors, air filters or separators to remove SO$_2$; however, a major drawback is high temperature needed [1-3]. Graphene, with its high surface area, is a potential material for use in SO$_2$ adsorption [3-5].

Some of the main application areas of graphene based fibers are;

- Filtration and seperation
- Sensors
- Catalysts
- Functional textiles
- Energy storage
- Nanotechnology
- EMI shielding

In this study, adsorption and desorption properties of graphene oxide (GO) fiber and GO fiber incorporated with PVA, were examined for their potential use in gas filters.
II. MATERIALS, METHODS AND PROCEDURES

A. Materials

Graphene-GIC (expandable, 30 μm thickness, 300 μm diameter, %99 purity) was obtained from Grafen Co., KMnO\textsubscript{4} (158.03 g/mol), H\textsubscript{2}SO\textsubscript{4} (98.08 g/mole) and HCl (37%) were supplied from Merck. NaNO\textsubscript{3} (84.99 g/mole) and PVA were provided by ZAG.

B. Methods and Procedures

Graphene oxide was produced from graphene oxide dispersion obtained by Modified Hummers method described in the studies by Ucar et al [6-8].

Natural graphite flakes), NaNO\textsubscript{3} and H\textsubscript{2}SO\textsubscript{4} were mixed and stirred uniformly in an ice bath with a magnetic stirrer. KMnO\textsubscript{4} was added to the mixture slowly and gradually. After the completion of KMnO\textsubscript{4} addition, the dispersion was stirred in the ice bath. Distilled water was added to the solution gradually to prevent any chemical risks. The reaction temperature was raised, distilled water and H\textsubscript{2}O\textsubscript{2} were added to the solution while the temperature is being lowered at the same time. H\textsubscript{2}O\textsubscript{2} addition was performed at once instead of gradual addition, as the solution was considerably diluted. Addition of H\textsubscript{2}O\textsubscript{2} turned the solution into a yellow – blackish color. The next day, the diluted top portion of the solution was decanted and splitted into centrifuge tubes evenly. Graphene oxide solution was washed with HCl solution in centrifuge (Nüve, NF800R) to remove impurities. For pH adjustment, the solution went through several washings with distilled water until the solution pH reached pH 5-6. Then, the solution is dispersed by mechanical homogenizer (WiseTis Homogenizer, HG-15D) to prepare the GO dispersion for production of GO fibers by wet spinning method.

The graphene oxide fibers were produced with wet spinning in three coagulation baths containing various amounts of ethanol and water. In order to obtain PVA incorporated GO fiber, 10% PVA was included to the last coagulation bath.

The coagulation bath conditions are shown in Figure 1 and the production process of the nonwoven surface discs is shown in Figure 2.

![Coagulation Conditions Diagram](image-url)
Fiber surface morphologies were characterized with QUANTA FEG 250 Scanning Electron Microscopy (SEM). Before SEM measurements, the samples were coated with Au/Pd. AFM analysis was performed with Ambios Technology, Santa Cruz, CA. A silicone nitrate tip was used with AFM-tapping mode. SO$_2$ adsorption capacities were analyzed by obtaining fiber web disc of GO fiber / PAN incorporated GO fiber in the last coagulation bath. Absorption and desorption measurements were performed by using a quartz reactor. The flow rate of SO$_2$ gas was set to 1.47 ml/min and for N$_2$ gas 150 ml/min for 60 minutes. Also, titration method was applied after desorption measurements to determine the maximum adsorption capacities. The surface area calculations were performed according to Brunauer-Emmett-Teller (BET) method. The pore size and surface area measurements were conducted with Quantachrome Quadrosorb SI instrument.

Fig 3. GO nonwoven surface
III. RESULTS

SEM images were used to characterize the surface morphologies and SEM images of the fibers are shown in Figure 4 and average electrical conductivity and AFM test results are shown in Figure 5 and Table 1 respectively.

![SEM images of GO fiber and PVA incorporated GO fiber](image1)

a) GO Fiber

![SEM images of GO fiber and PVA incorporated GO fiber](image2)

b) PVA incorporated GO Fiber

Fig. 4. SEM images of GO fiber and PVA incorporated GO fiber

![Electrical conductivity test results](image3)

![Electrical conductivity test results](image4)

Fig 5. Electrical conductivity test results
TABLE 1. AFM test results

| Sample                  | Rpv (μm) |
|-------------------------|----------|
| GO Fiber                | 4.963    |
| PVA incorporated GO Fiber | 3.238   |

It is evident from both SEM images and Rpv values that the surface roughness decreases with the incorporation of PVA. As PVA itself is not as conductive as GO, when PVA is incorporated to GO fibers, the electrical conductivity also is not affected clearly by the addition PVA since both of sample has $10^{-3}$ S/cm.

TABLE 2. BET test results

| Sample                  | Surface area (m²/g) | Average pore diameter (nm) | Total pore volume (cc/g) |
|-------------------------|---------------------|---------------------------|-------------------------|
| GO Fiber                | 24.971              | 5.399                     | 3.37*10⁻²                |
| PVA incorporated GO Fiber | 7.056              | 1.128                     | 1.99*10⁻²                |

BET results are shown in Table 2. As can be seen, incorporation of PVA reduces the surface area, total pore volume and average pore diameter.

In order to measure SO₂ adsorption capacity, fibers are spun in a continue fiber set-up and nonwoven surface discs were obtained.

The SO₂ adsorption test results are shown in Figure 6

![Fig 6. The SO₂ adsorption test results](image)

As can be seen in Figure 6, addition of PVA increased SO₂ adsorption properties of nonwoven discs that might be because of PVA related functional groups PVA. In the literature, the adsorption capacity of nanosized GO was found to increase with reduced temperature, and measured 325 mg/g at highest at 15 °C [9].
IV. CONCLUSION

In this study, effect of PVA incorporation on SO₂ adsorption properties of GO fibers was investigated. It is found that addition of PVA reduces the surface roughness, surface area, average pore size and pore volume. There is no significant effect of PVA on electrical conductivity, however the effect of PVA on SO₂ adsorption is significant, leading to higher SO₂ adsorption.

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