Impact of Thermal Treatment on Adsorption Properties of Graphene-Based Materials

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***Abstract*—**Sulfur dioxide (SO_2) is a very toxic air pollutant gas and it causes the greenhouse effect, photochemical smog, and acid rain, which threaten human health severely. Thus, the capture of SO_2 gas is very important for the environment. Graphene which is twodimensional material has excellent mechanical, chemical, thermal properties, and many application areas such as energy storage devices, gas adsorption, sensing devices, and optical electronics. Further, graphene oxide (GO) is examined as a good adsorbent because of its important features such as functional groups (epoxy, carboxyl and hydroxyl) on the surface and layered structure. The SO_2 adsorption properties of the fibers are usually investigated on carbon fibers. In this study, potential adsorption capacity of GO fibers was researched. GO dispersion was first obtained with Hummers' method from graphite, and then GO fibers were obtained via wet spinning process. These fibers were converted into a disc shape, dried, and then subjected to SO_2 gas adsorption test. The SO_2 gas adsorption capacity of GO fiber discs was investigated in the fields of utilization of different coagulation baths and reduction by hydrazine hydrate. As coagulation baths, single and triple baths were used. In single bath, only ethanol and $CaCl_2$ (calcium chloride) salt were added. In triple bath, each bath has a different concentration of water/ethanol and $CaCl_2$ salt, and the disc obtained from triple bath has been called as reference disk. The fibers which were produced with single bath were flexible and rough, and the analyses show that they had higher SO_2 adsorption capacity than triple bath fibers (reference disk). However, the reduction process did not increase the adsorption capacity, because the SEM images showed that the layers and uniform structure in the fiber form were damaged, and reduction decreased the functional groups which SO_2 will be attached. Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR), X-Ray Diffraction (XRD) analyzes were performed on the fibers and discs, and the effects on the results were interpreted. In the future applications of the study, it is aimed that subjects such as pH and additives will be examined.

***Keywords*—**Coagulation bath, graphene oxide fiber, reduction, SO_2 gas adsorption.

I. Introduction

SULFUR dioxide (SO_2), a colorless, malodorous, and poisonous gas, can be produced by domestics, factories, or volcanoes [1]. It causes greenhouse effect, photochemical smog [2], furthermore, can react with oxygen and water to form sulfuric acid that induces acid rains [3]. Accordingly, reductions of sulfur sources may yield benefits in air quality.

One of the SO_2 removal ways is an adsorption, and adsorption capacities of carbon based materials are intensively investigated. As a fiber form, activated carbon fibers are generally studied [3]-[7]. As far as is known, there is not enough research about GO fiber's SO_2 adsorption capacity. Because of the functionalizable surface area of the material, porosity, the oxygen-containing groups on the surface, and chemical stability makes GO an acceptable adsorbent material [2], [8].

The aim of the present study is to understand the influences of coagulation bath content and reduction treatment of fiber on SO_2 adsorption capacity. The fiber drawing process was done by wet spinning method. A portion of the product was produced in a triple coagulation bath and then reduced with hydrazine. The other part was produced with a single coagulation bath. Afterwards, SEM, XRD, FTIR, and SO_2 adsorption analyzes were done to see the effects.

II. Methods

A. Synthesis of GO Fibers and Discs

Thermal exfoliation of expandable graphite-GIC (thickness: 30 µm, diameter: 300 µm) was applied at 1020 ºC for 35 s under argon gas. Then, GO was synthesized by Hummers' method [9]. Briefly stated, graphite, sodium nitrate ($NaNO_3$), sulfuric acid (H_2SO_4) materials were stirred together. By controlling temperature with ice bath, potassium permanganate ($KMnO_4$) was added. Following by stirring, heating and cooling processes, distilled water was added. Suspension was kept wait for five days. Then, suspension was mixed with hydrogen peroxide (H_2O_2). The day after, graphitic oxide is obtained by centrifugation with hydrogen chloride (HCl) and distilled water until pH 3. After mechanical homogenization step, it was called GO dispersion.

The fibers were produced by the wet spinning method (at a feed rate of 20 ml/h) from GO dispersion and passed through coagulation baths (Table I). Then, the fibers were placed in an empty container of 3.2 cm diameter to cover the entire substrate. Drying process was done in room conditions. The produced disc (weights should not be less than 0.1 gram) conforms to other processes and tests (Fig. 1).

TABLE I
Coagulation Bath Types

Bath Type	Content
First coagulation bath of triple coagulation	30 ml/70 ml (ethanol/water) + 5 wt.% $CaCl_2$
Second coagulation bath of triple coagulation	40 ml/60 ml (ethanol/water)
Third coagulation bath of triple coagulation	50 ml/50 ml (ethanol/water)
Single coagulation bath	100 ml ethanol + 5 wt.% $CaCl_2$

Fig. 1 GO disc shape

B. Reduction of GO Discs

Reduction was carried out by dipping fibers and discs in hydrazine hydrate (N_2H_5OH) solution. For this process, 5 ml of hydrazine hydrate was placed on the petri dish and placed in the samples and allowed to interaction for 20 minutes. Before subjecting to the SO_2 absorption test, the product was dried at 80 °C for 2h to evaporate the residual hydrazine.

The fibers which were produced from triple coagulation bath without any treatment and treated with hydrazine hydrate were called reference sample and reduced sample, respectively.

C. Adsorption of SO_2

Adsorption process consists of three successive stages: Adsorption, desorption, and titration.

Adsorption: The sample in the quartz tube inside the tube furnace is placed perpendicular to the incoming gas stream. Subsequently, the tube was fed with N_2 gas at 150 ml/min and SO_2 gas at 1.47 ml/min during 1h.

Desorption: Feeding of 150 ml/min N_2 gas was continued. The SO_2 gas was turned off. For a while, the N_2 gas feed was continued without processing to allow SO_2 to move away from the medium. Desorption was achieved by keeping the oven at 360 °C for 60 minutes after reaching 360 °C at a rate of 5 °C/min, and thereby releasing the SO_2 trapped by the sample. The gas leaving the sample is trapped by a gas-flushing bottle placed in the gas outlet line and containing 5% of a 100 ml
H_2O_2 solution. Here, SO_2 reacts with water to form H_2SO_4. The amount of sulfuric acid formed after desorption of the SO_2 gas was determined by titration.

Titration: The amount of H_2SO_4 which is present in the solution after desorption is determined by titration method, and the amount of SO_2 adsorbed by the sample is calculated by molar calculation method.

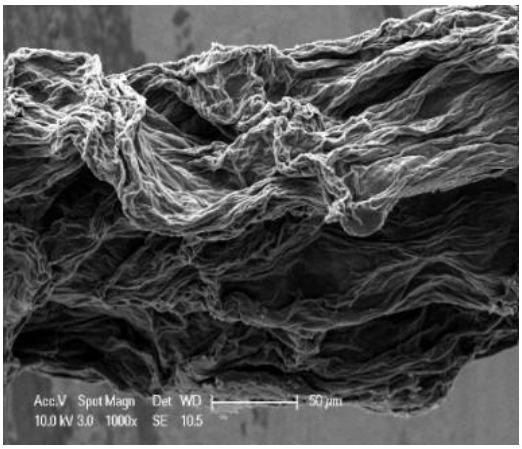
During the titration, 0.1 N H_2SO_4 and 0.1 N sodium hydroxide (NaOH) were used for the calibration. In addition, 0.1 N NaOH was used for titration of the H_2O_2 solution. A 1ml pipette scaled in 0.01 ml increments was used to increase the sensitivity of the assay. The volume of NaOH solution titrating the H_2O_2 solution relative to the amount of NaOH solution titrating H_2SO_4 was proportioned, and the SO_2 adsorption capacity is determined.

D. Testing and Characterization

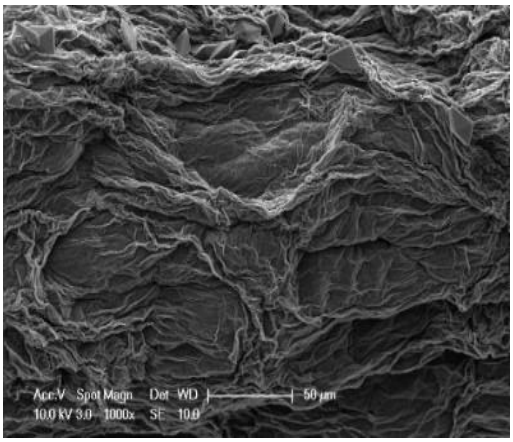
The morphology and the microstructure of samples were observed by SEM (QUANTA FEG 200). FTIR spectra were recorded by using Perkin Elmer FT-IR C99089. XRD patterns were obtained with PW3040 diffractometer using Cu Kα radiation (λ=1.5405 Å).

III. Results and Discussion

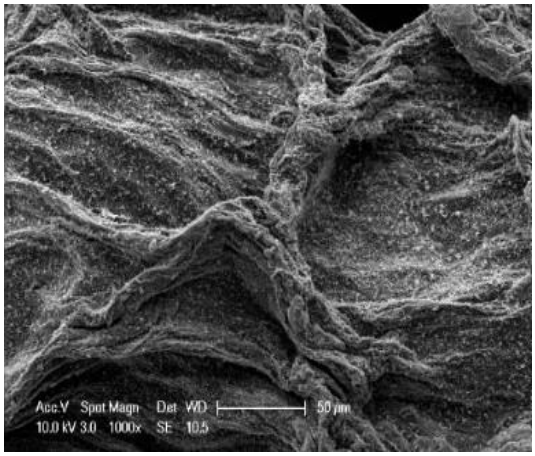
SEM analyzes was performed to observe fiber structure after treatments. SEM morphology figures (Fig. 2) show that reduced sample and single coagulation bath sample are swollen. Although all SEM images were taken at the same magnification, these samples did not fit the picture. Besides, reduced sample lost its roughness. The white particles on the single coagulation bath sample may be from $CaCl_2$ salt.



(a)



(b)



(c)

Fig. 2 SEM morphology of fibers, longitudinal appearances of (a) reference sample, (b) reduced sample, (c) single coagulation bath sample

In FTIR spectra (Fig. 3), the broad peak between 3000- 3700 cm^{-1} belongs to the O-H bond stretching in the hydroxyl group, the peaks at 2984 cm^{-1} and 2881 cm^{-1} belong to the stretching vibrations of symmetric and antisymmetric CH_2, respectively. The weak peak at 1700 cm^{-1} belongs to the C = O bond stretching of the carbonyl and carboxyl groups. The peaks at 1587 cm^{-1}, 1365 cm^{-1}, and 1036 cm^{-1} belong to C=C bonds of aromatic structures, C-OH stretching bonds and C-OC stretching bonds of epoxy groups, respectively. Very small vibrations at 976 cm^{-1} refer to other epoxy, ether and peroxide groups in the structure [10]-[12]. For reduced sample, the disappearance of oxygenated functional groups is consistent with the disappearance of the peaks. Also from XRD analyzes, GO peaks are observed at (2 Theta: 10°) for reference sample and single coagulation bath sample but reduced sample shows graphite peak (2 Theta: 26.5°) after hydrazine hydrate treatment. As seen from Figs. 3 (a) and (c), reference and single coagulation bath samples show almost same FTIR spectra.

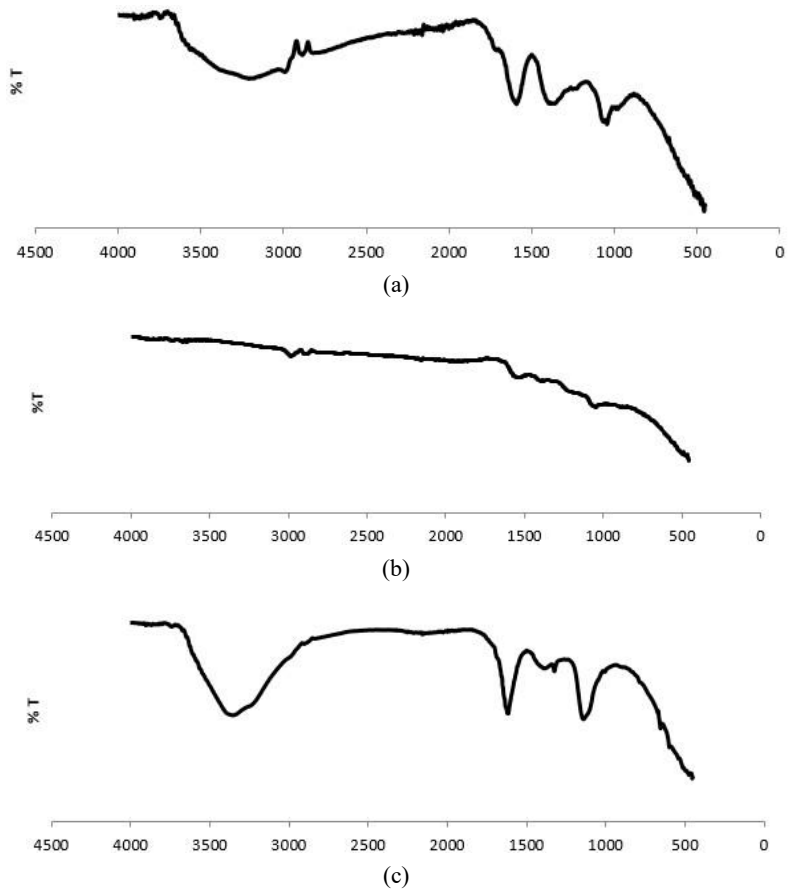


Fig. 3 FTIR spectra of fibers (a) reference sample (b) reduced sample, (c) single coagulation bath sample

TABLE II
COMPARISON OF SO_2 ADSORPTION CAPACITIES

Sample	SO_2 adsorption capacity (mg SO_2 / 1 g sample)
Reference sample	311.69
Reduced sample	270.58

As it is seen from Table II, single coagulation bath sample

IV.	Single bath sample	379.17

CONCLUSION

GO fibers were produced from wet spinning method at single and triple baths. Then, triple coagulation bath fibers were treated with hydrazine hydrate. The effects on SO_2 adsorption of these fiber groups were studied. The adsorption capacity of the single-bath production was found to be higher than the reference sample and the reduced fiber was found to be less.

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