

# Effect of Heat Treatment on CO<sub>2</sub> Adsorption of Ammonized Graphite Nanofibers

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## Abstract

In this work, graphite nanofibers (GNFs) were prepared by ammonia and heat treatment at temperatures up to 1000°C to improve its CO<sub>2</sub> adsorption capacity. The effects of the heat treatment on the textural properties and surface chemistry of the GNFs were investigated by N<sub>2</sub> adsorption isotherms, XRD, and elemental analysis. We found that the chemical properties of GNFs were significantly changed after the ammonia treatment. Mainly amine groups were formed on the GNF surfaces such as lactam groups, pyrrole and pyridines. The GNFs treated at 500°C showed highest CO<sub>2</sub> adsorption capacity of 26.9 mg/g at 273 K in this system.

**Keywords :** CO<sub>2</sub> adsorption, Graphite nanofibers, Ammonia, Heat treatment

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## 1. Introduction

Recently, the researchers have reported that global CO<sub>2</sub> emissions from fossil fuels increased 29% between 2000 and 2008 and 41% from 1990~2008, and the current concentration of CO<sub>2</sub> in the atmosphere is now at its highest in at least 2 million years, according to a new study in the journal Nature Geoscience [1]. Thus, reducing CO<sub>2</sub> emissions as a global environmental problem has been paid more and more attention.

Current or proposed methods of CO<sub>2</sub> capture from flue gas include absorption, adsorption, cryogenic distillation, and membrane separation. However, commercial CO<sub>2</sub> capture technology that exists today is very expensive and energy intensive. Improved technologies for CO<sub>2</sub> adsorption are necessary to achieve low energy penalties [2]. The CO<sub>2</sub> adsorption is typically used at a final polishing step in a hybrid CO<sub>2</sub> capture system [3]. Up to now, different types of adsorbents have been used in CO<sub>2</sub> capture, such as zeolites, alumina, mesoporous silica, CaO, porous carbons [4-8]. Especially, porous carbons were used in CO<sub>2</sub> separation due to their highly developed porosity, an extended surface area, surface chemistry, and thermal stability. Previous studies toward the use of activated carbons, activated carbon fibers, carbon molecular sieves, carbon nanotubes as an adsorbent for CO<sub>2</sub> capture [9-11].

Graphite nanofibers (GNFs) as one of the most important carbon materials, which have been attracted much attention due to their novel properties such as high aspect ratio, small radius of curvature, high mechanical strength, unique

electrical properties, and chemical stability [12]. Therefore, these properties that make them potentially useful in many applications as gas storage, electrodes, filler, and catalyst supports [13-16]. However, the studies of CO<sub>2</sub> adsorption on GNFs are still very limited in the literature. This is due to that the specific surface area of GNFs is lower compared with other carbon materials. CO<sub>2</sub> adsorption generally depends on their physical and chemical properties. Physical properties of carbons include their specific surface area, size, and porosity, whereas chemical properties are mainly determined by their surface functional groups, including carboxyl, carboxylic anhydrides and so on [17]. To date, several methods have been used in order to obtain porous GNFs, including the activation at high temperature with CO<sub>2</sub> or a water steam stream and a chemical activation method [18-20].

In the present work, we focused on the preparation of porous and ammonized GNFs, in order to improve the CO<sub>2</sub> adsorption capacity of GNFs. The GNFs with different physical structures were prepared by ammonia and heat treatment at temperatures up to 1000°C, and their physico-chemical properties and CO<sub>2</sub> adsorption capacity were investigated.

## 2. Experimental

### 2.1. Materials and Sample Preparation

The GNFs (straight type, Nanomirae Co.) were activated with HNO<sub>3</sub> for 12 h at 60°C. The 10 g of activated GNFs

were dispersed in 50 ml of ammonia solution by mechanically stirring the mixture for 24 h at 60°C and then filtered and dried 24 h at 60°C. The sample was denoted as GNF-A. About 2 g of ammonized GNFs were placed in a quartz tube reactor, heated at 10°C/min to 500°C, 700°C, 900°C, and 1000°C, in N<sub>2</sub> flow and keep for 2 h, and the obtained samples were denoted as G-A-500, G-A-700, G-A-900, and G-A-1000, respectively. This work employed carbon nanotubes (CNTs) purchased from Nano Solution Co. (CNTs with a diameter of 10~25 nm).

## 2.2. Characterization

The pH of the sample was evaluated according to ASTM (American Society for Testing and Materials) Standard Procedure D 3838. Samples of 0.5 g were added to 20 ml of distilled water and suspensions were stirred overnight to reach equilibrium. The changes in chemical composition of the GNFs surfaces were analyzed by elements analyzer (Thermo EA1112). Then, the samples were filtered and pH of the solution was measured.

N<sub>2</sub>/77 K full isotherms were measured using an ASAP 2010 (Micromeritics). Before the measurement, the samples were degassed at 200°C for 12 h to obtain a residual pressure of less than 10<sup>-6</sup> mm Hg. The N<sub>2</sub> adsorbed on the GNFs was used to calculate the specific surface area by means of a BET (Brunauer–Emmett–Teller) equation. The total pore volume was estimated to be the liquid volume of the nitrogen at a relative pressure of about 0.995, and the micro- and mesopore structures were analyzed using D-R (Dubinin–Radushkevich) and BJH (Barrett–Joyner–Halenda) equations, respectively. Wide-angle X-ray diffraction (XRD) patterns of the GNFs were obtained with a Rigaku Model D/MAX-III B diffraction meter equipped with a rotation anode using CuKα radiation ( $\lambda=0.15418$  nm). The CO<sub>2</sub> adsorption property of GNFs was characterized by surface area analyzer (BEL, Japan) at 273 K in this system (1 atm). Before each analysis, samples were degassed for 12 h at 200°C.

## 3. Results and Discussion

Table 1 shows the textural properties of the GNFs before and after treatments. It was observed that the pore structure of GNFs and treated GNFs does not change much due to modification by either ammonia treatment or heat treatment. The specific surface areas of GNFs decreased after treated with ammonia. The small changes in the pore structure are attributed to creation of functional groups such as lactam groups, pyrrole and pyridines [21]. It was found that the specific surface area the fractions of micropore increased to G-A-500, but then showed a decrease at G-A-1000. It can be seen that the micropores were mainly enhanced in the lower temperature, but, the mesopore volume was increased in the

**Table 1.** Pore structure parameters for the GNFs before and after treatments

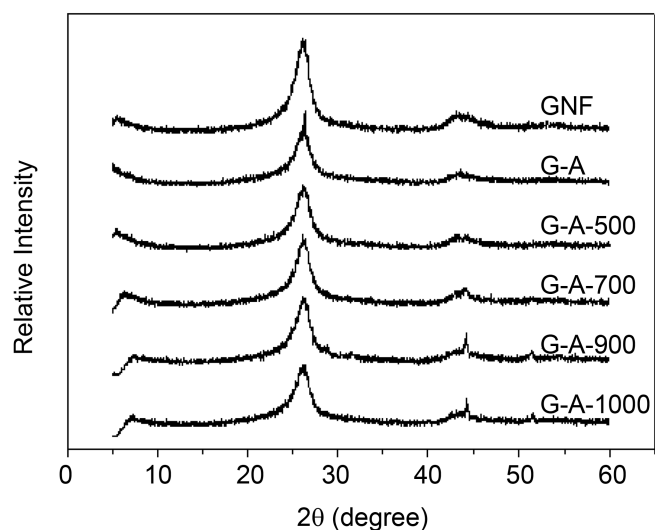
Samples	S <sub>BET</sub> <sup>a</sup> (m <sup>2</sup> /g)	V <sub>M</sub> <sup>b</sup> (cm <sup>3</sup> /g)	V <sub>T</sub> <sup>c</sup> (cm <sup>3</sup> /g)	F <sub>M</sub> <sup>d</sup> (%)	Pore Size (nm)
GNF	150	0.013	0.273	4.8	6.7
GNF-A	143	0.013	0.283	4.6	7.1
G-A-500	180	0.016	0.295	5.4	7.0
G-A-700	179	0.016	0.301	5.3	7.1
G-A-900	152	0.015	0.268	5.6	6.9
G-A-1000	138	0.013	0.264	4.9	7.1

<sup>a</sup> Specific surface area (m<sup>2</sup> g<sup>-1</sup>): BET equation ( $p/p_0 = 0.05 \sim 0.1$ ).

<sup>b</sup> Micropore volume (cm<sup>3</sup> g<sup>-1</sup>): D-R equation,  $V_{\text{intercept}} \times 0.001547$ .

<sup>c</sup> Total pore volume (cm<sup>3</sup> g<sup>-1</sup>):  $V_{\text{ads}}(P/P_0 = 0.995) \times 0.001547$ .

<sup>d</sup> Fraction of micropore (%):  $V_m/V_T \times 100$ .



**Fig. 1.** XRD patterns of the GNFs before and after treatments.

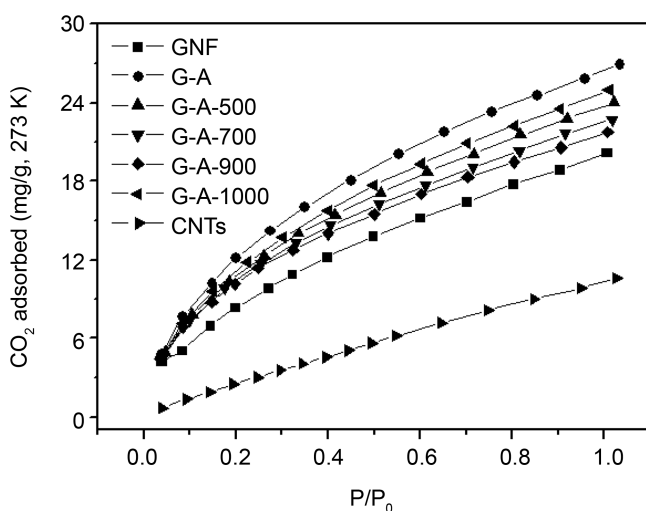
higher temperature. Yoon *et al.* reported that micropore development is correlated with the partial opening of graphite layers in GNFs [22]. According this view, micropore development at lower temperatures (500, 700°C) can indeed result from the opening of graphite layers. However, the mesoporous development at 1000°C is probably due to the breaking of GNFs [23,24].

Fig. 1 shows the XRD patterns of the GNFs before and after treatments. It reveals that the peaks were explicable in terms of the known structure of the graphite at  $2\theta=26.1^\circ$  (002) and  $43.1^\circ$  (101) peaks. It show also the presence of metal catalysts peaks at  $2\theta=44.3^\circ$  (111) and  $51.4^\circ$  (200) peaks. The graphite peak (002) intensity gradually decreases with increasing temperature, probably because higher temperature affects the graphene layer structures of GNFs. In the case of G-A and G-A-500, the XRD patterns have not significantly change.

The elemental compositions as determined by elemental

**Table 2.** Elemental analysis and pH values of the GNFs before and after treatments

Samples	O (%)	N (%)	pH
GNF	1.35	0.58	6.88
GNF-A	4.04	4.52	8.18
G-A-500	2.16	2.79	7.72
G-A-700	0.86	1.79	7.46
G-A-900	0.76	0.93	7.21
G-A-1000	0.56	0.64	7.07

**Fig. 2.** Carbon dioxide adsorption behaviors of the pristine GNFs, treated GNFs, and CNTs measured at 273 K.

analysis are presented in Table 2. It appears that ammonia treatment yields a lower content of nitrogen. The nitrogen content decreases with increasing treatment temperature, reaching a maximum at 500°C and 700°C. The reaction of ammonia with carbon can be expected to take place at acidic sites, formed mainly by surface acidic functional groups as carboxylic groups [25]. This is due to that the nitrogen-containing functional groups such as lactams, imide, and amides may be formed from ammonia by mild conditions (500, 700°C) and can be desorbed at high temperature (1000°C). The acid and basic character of GNFs are assessed by the pH values and also shown in Table 2. It shows that the pH values of ammonia treated GNFs decreased with increasing treatment temperature. This means that the types of chemical nitrogen fixation by GNFs: nitrogen bound to the carbon as aside group, such as an nitrogen functional group, nitrogen chemically bound on the carbon surface as a lactam, or pyridine-pyrrole-like group and as a nitrile.

The CO<sub>2</sub> adsorption capacities were measured by CO<sub>2</sub> adsorption isotherms at 273 K (1 atm). The commercial CNTs with surface areas of 230 m<sup>2</sup>/g and CO<sub>2</sub> adsorption capacities of 10.6 mg/g, and the GNFs was able to achieve 20.2 mg/g of CO<sub>2</sub> adsorption capacities (Fig. 2). It is clear

that GNFs show better performance compare with CNTs. As shown in Fig 2, the ammonia treated GNFs present better performance for CO<sub>2</sub> adsorption than the pristine GNFs. The behavior of the ammonia treated GNFs to adsorb CO<sub>2</sub> should be related to the number and availability of amine groups for reaction [15,16]. As described by Mangun *et al.* [24], the modification of activated carbon fibers (ACFs) with dry ammonia from 500 to 800°C for different periods of time leads to a formation of new nitrogen-containing groups in the fibers. The formation of carbamate is favored in the manner shown in Eqs. ((1), (2), and (3)). Two moles of amine groups react with 1 mol of CO<sub>2</sub> molecule [26].



In addition, the gas adsorption is greatly depended on the micropores of carbon materials. Therefore, the highest CO<sub>2</sub> adsorption capacity of 26.9 mg/g is shown for the GNFs treated with ammonia in low temperature (500°C). This result clearly indicates that ammonia and heat treatment leads to increase of the affinity of GNFs towards CO<sub>2</sub>.

#### 4. Conclusions

In this work, the commercial GNFs with different physical structures were prepared by ammonia and heat treatment at temperatures up to 1000°C to improve its CO<sub>2</sub> adsorption capacity. We found that the ammonia treatment introduced nitrogen-functionalities into the surface of GNFs, which resulting in increasing their CO<sub>2</sub> adsorption capacity. In addition, the heat treatment led to an improvement of the microporosity of GNFs at lower temperature. The GNFs treated at 500°C showed highest CO<sub>2</sub> adsorption capacity of 26.9 mg/g at 273 K in this system. We concluded that in order to obtain a high CO<sub>2</sub> adsorption capacity, two key conditions are required: well-defined microporosity and well-developed basic functional groups of the solid surfaces studied.

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