

STRUCTURAL CHANGE OF CARBON NANOFIBERS BY KOH ACTIVATION

Yan Song, Wenming Qiao, Seong-Ho Yoon, Yozo Korai, Isao Mochida
Institute of Materials Chemistry and Engineering, Kyushu-u University

Corresponding author e-mail address: songyan@cm.kyushu-u.ac.jp

1. INTRODUCTION:

Carbon nanofiber (CNF) has many potential applications such as catalyst or catalyst support, selective adsorption agents, and energy storage and so on for its particular nano-structural properties. However, the low surface area of CNF restricts its applications. So, CNF with high surface area is expected.

Chemical activation with alkali compounds such as KOH is a well-known method to prepare activated carbon materials with high surface area[1-3]. Recently, carbon nanotube (CNT) was activated by KOH and NaOH to develop the porosity in CNT for its new applications[4,5].

In this paper, CNF was activated by KOH to develop surface area and porosity. Structure change of the CNFs was studied by using N₂ adsorption, XRD, SEM and TEM. On this basis, the mechanism of KOH activation of CNF was illustrated.

2. EXPERIMENTAL:

2.1 Preparation of high surface area CNF

Herringbone-type CNF was used in the experimental. The pore structure of CNF was listed in Table 1. The KOH activation process was as followed: Firstly KOH was dissolved in ethanol, secondly CNF was added in the solution, and then the solution was stirred for 50min, next the mixture was put into the oven to vaporize the ethanol, and finally the homogeneous mixture of CNF and KOH was got. Put the mixture into a Ni-pan, which was placed in a stainless steel tube reactor and then heated by a standing furnace. Activation conditions were 800-1000°C for 1h with a heating rate of 5°C /min in argon flow of 60ml/min. The activated product was washed with distilled water, filtered and dried at 105°C.

2.2 Characterization of CNFs

BET surface area and total pore volume were calculated using Nitrogen adsorption at 77K using a Sorptomatic 1990 instrument. Before adsorption the samples were outgassed at 200°C for 12hr until constant weight. The crystalline parameters such as d002 and Lc were measured by using X-ray diffractometer (Rigaku, CuK α target). Scanning electron microscopy (SEM) images were obtained by means of JSM-6320F instrument which was operated at 10KV in the secondary electron imaging mode. Transmission electron imaging was performed on a JEM 2100F microscope operated at 200KV. The sample was prepared by dispersing the extracted fibers in 1-butanol[6]. The imaging was enabled by depositing a few drops of the suspension on a carbon-coated, 400 mes, copper grid. The solvent was allowed to evaporated before imaging.

3. RESULTS:

3.1 Pore structural change of CNF after KOH activation

Table 1 revealed the influence of activation temperature on the properties of CNFs. The activation yield decreased with the increasing of activation temperature, while surface area and pore volume increased with the increasing of activation temperature firstly, reached

maximum at 950°C, and then decreased slightly. The maximum of surface area and pore volume of the resultant CNF were 1258 m²/g and 1.141 cm³/g, respectively.

Nitrogen adsorption isotherms of CNFs were showed in Fig.1. The adsorption isotherms of cnf and its activated forms were Type IV, having a marked hysteresis, which belong to mesoporous carbons. With the improvement of activation degree, the hysteresis loop enlarged. That is to say, the content of mesopore increased as the enhancement of surface area. Fig.2 gave the BJH pore distribution of these CNFs. It can be seen that cnf and its activated forms have strong pore distribution at about 2nm and 4nm.

3.2 Morphology of CNF and its activated forms

Fig.3 and Fig.4 showed SEM and TEM morphologies of CNF and its activated forms, respectively. It can be observed clearly that nanofiber became short after activation, and with the increase of the activation degree, this trend became more clearly. But the fiber form still remained (Fig.3e and 3f) on the whole even if CNF with BET surface area of 1258 m²/g. At more severe activation condition (activation temperature was 1000°C), the fiber became into particle (Fig.3g), and the alveolate shape (Fig.3h) appeared. From TEM photographs, CNF carried the herringbone-type alignment of graphene sheets, which are angled to some extent against the fiber's axis as shown in Fig.4b. Some ladder-like structures appeared after activation (Fig.4c, Fig.4e and Fig.4g). At moderate activation (Fig.4c- Fig.4f), the herringbone-type alignment was still totally remained. When the activation temperature increased to 950°C, the nanofiber structure began to collapse to some extent (Fig.4i and Fig.4j) though some nanofibers (Fig.4g and Fig.4h) still remained. When the activation temperature researched 1000°C, the nanofiber structure was totally disappeared and the amorphous carbon (Fig.4k and Fig.4l) formed. At the same time, some capsule-like structure (Fig.4m and Fig.4n) appeared, which was coincided with the SEM results (Fig.3h). Simultaneity, it can be seen that the interlayer distances between graphene sheets of CNF were enlarged after KOH activation.

3.3 XRD properties of CNF and its activated forms

Fig.5 showed the XRD properties of CNF and its activated forms. The crystallinity of CNF decreased after KOH activation, for its d002 interspacing increased and Lc(002) value decreased.

4. DISCUSSION:

It is well known that chemical activation using KOH or NaOH generally generates activated carbon with a high surface area over 2000m²/g, and especially, precursors with structural disordered carbons were easily activated using this method. Graphite is difficult to develop the porosity by activation for it contains ordered structure [7]. Activation will decrease the ordered structure and may lead to the structural rearrangement. So, activation conditions should be choosed carefully to avoid the structural collapse of CNF.

A generally accepted KOH activation mechanism is that KOH dehydrates to transform into K₂O at 400°C and the resultant K₂O is reduced into metallic potassium by carbon at high temperature, and then metal K intercalates into graphite structures to develop the porosity after the activated product is washed.

There has some consistency between the morphology observation and XRD data of CNF. The TEM results showed clearly the broadening of interspacing between graphite layers along the fiber axis after activation. The XRD data showed a broadening of interspacing from 0.3416 to

0.3606 nm after CNF was KOH-activated at 900°C for 1h. SEM results showed that CNF became short after KOH activation, leading to the increase of the area of the edge carbon, which will add the surface area slightly. Metal K, occurred in the process of activation, intercalated into graphite structures. The interspacing between graphite layers was broadened in some parts, and the fiber was tailored into short one in the other parts.

On this basis, KOH activation mechanism of CNF was illustrated as followed: Amorphous carbon on the surface of CNF was firstly burnt and metal K was intercalated into nano-units that assemble to form CNF. The intercalation led to some separation and distortion of nano-units to develop the porosity of CNF, which will increase defects in ordered structure and decreased the crystallibility of graphene layers. So, d_{002} was enlarged and ladder-like structures were found in its morphology. In severe activation conditions, K was intercalated into graphene layers of nano-unit, which will result in the destruction and rearrangement of the graphene alignments into amorphous carbon.

5. CONCLUSION:

KOH activation was effective to increase the surface area of CNF. Activation separated and distorted the nano-units of CNF to introduce additional porosity. CNF with a surface area of 866m²/g, which still remained nanofiber morphology though some long fibers became short to some extent, could be obtained by choosing proper activation condition.

Acknowledgements

The authors thank JST (Japanese Science and Technology Agency) for financial support.

References:

- [1] Marsh H, Yan DS, O'Grady TM, Wennerberg A. Carbon 1984;22(6):603-611.
- [2] Qiao Weiming, Ling Licheng, Zha Qingfang, Liu Lang. Materials Science 1997;32: 4447-53.
- [3] Otawa T, Nojima Y, Miyazaki T. Carbon 1997;35(9):1315-1319.
- [4] Raymundo-Pinero E, Azais P, Cazorla-Amoros D, Linares-Solano, Szostak K, Beguin F. Extended abstract (No.13.1). Carbon'03 in Spain (2003).
- [5] Raymundo-Piñero E, Cazorla-Amorós D, Linares-Solano A, Delpeux S, Frackowiak E, Szostak K, Béguin F. Carbon 2002;40(9):1614-7.
- [6] P. V. Adhyapak, Trupti Maddanimath, Sushama Pethkar, et.al. Application of electrochemically prepared carbon nanofibers in supercapacitors, Journal of power Sources, 2002,109,105-110
- [7] Macia-Agullo JA, Moore BC, Cazorla-Amoros D, Linares-Solano. Extended abstract (No.3.29). Carbon'03 in Spain (2003).

Table1. Influence of temperature on the properties of CNFs

Sample	Temperature(°C)	Yield(%)	S _{BET} (m ² /g)	V _{total} (cm ³ /g)	V _{meso} (cm ³ /g)
CNF	----	----	300	0.447	0.560
CNF-H1	800	86	548	0.556	0.470
CNF-H2	850	80	760	0.695	0.670
CNF-H3	900	76	866	0.773	0.646
CNF-H4	950	71	1258	1.141	0.854
CNF-H5	1000	53	1212	1.139	1.061

Activation time: 60min; Ratio of KOH/CNF: 4/1; in Ar gas.

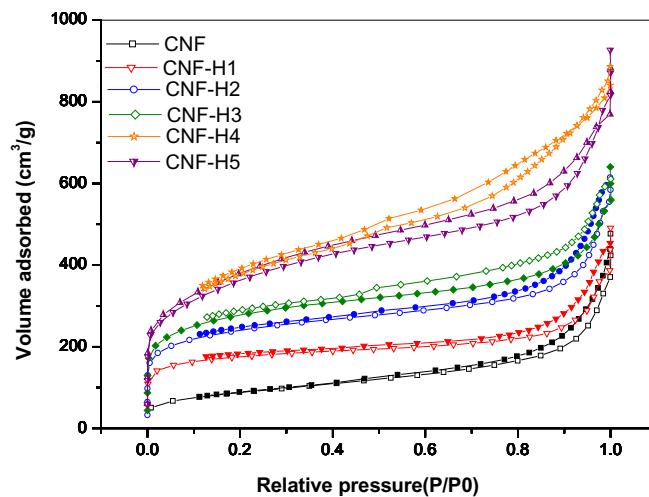


Fig.1 Nitrogen adsorption isotherms of CNFs

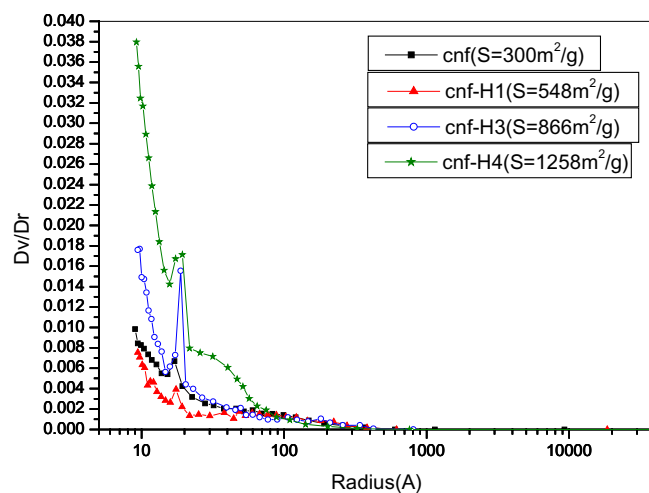
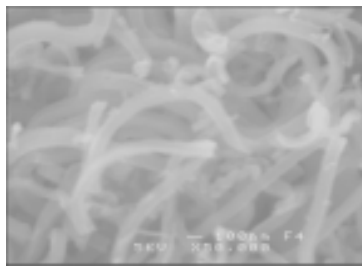
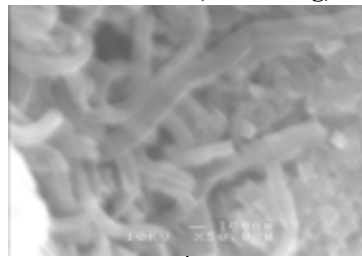


Fig.2 BJH pore distributions of CNFs



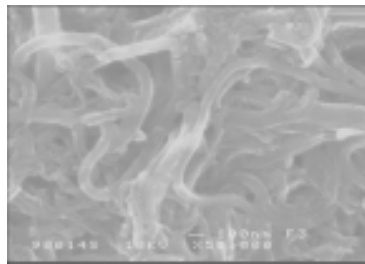
a

CNF(S=300m²/g)

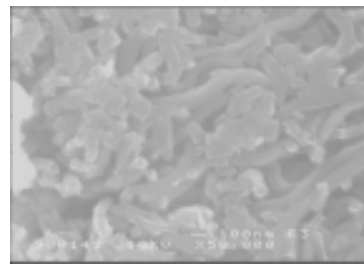


b

CNF-H1(S=548m²/g)

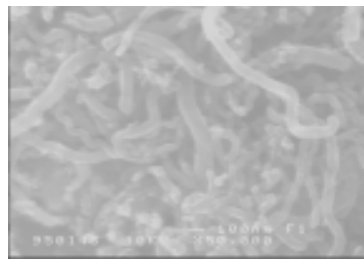


c

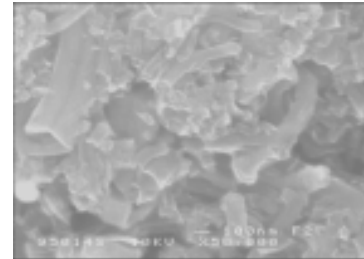


d

CNF-H3(S=866m²/g)

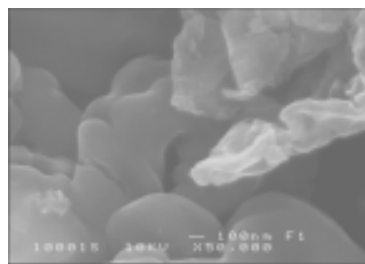


e

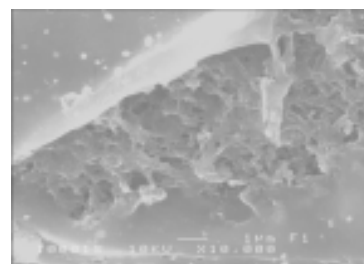


f

CNF-H4(S=1258m²/g)



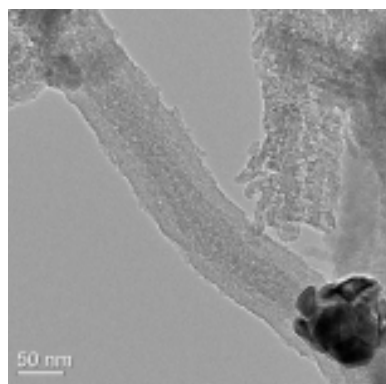
g



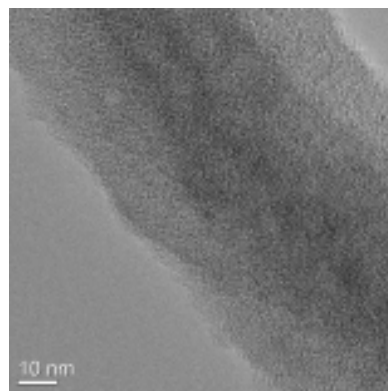
h

CNF-H5(S=1212m²/g)

Fig.3 SEM morphologies of CNF and its activated form

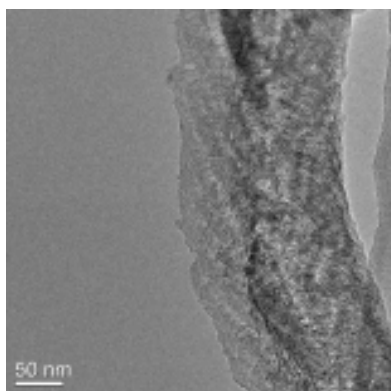


a

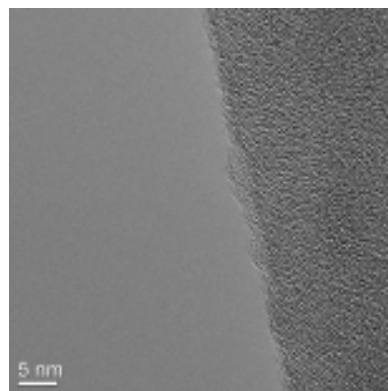


b

CNF(S=300m²/g)

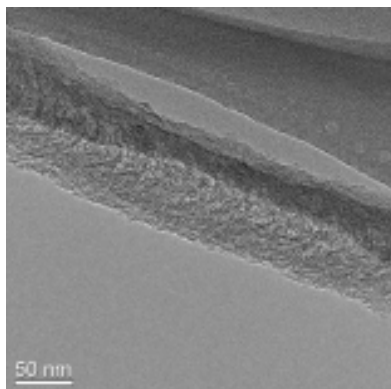


c

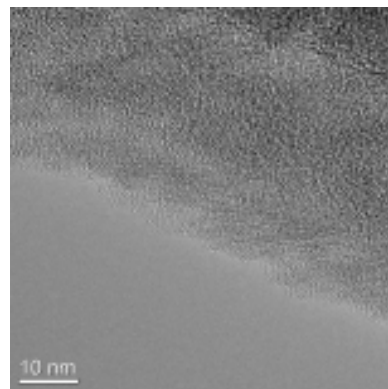


d

CNF-H1(S=548m²/g)

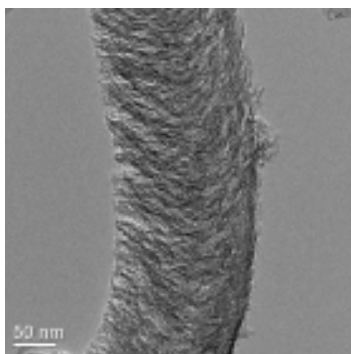


e

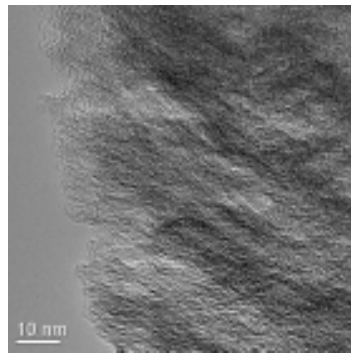


f

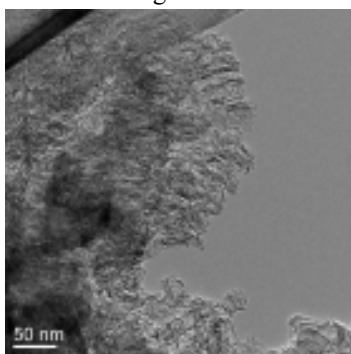
CNF-H3(S=866m²/g)



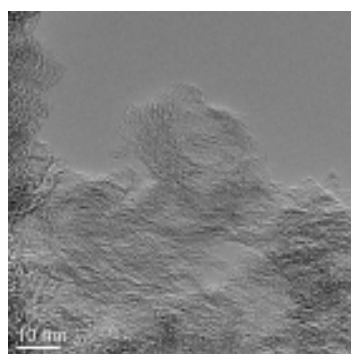
g



h

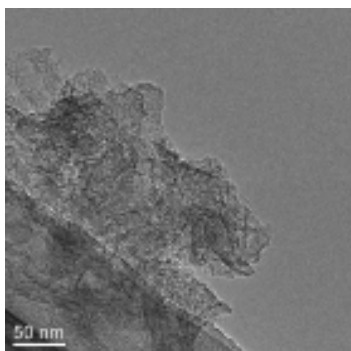


i

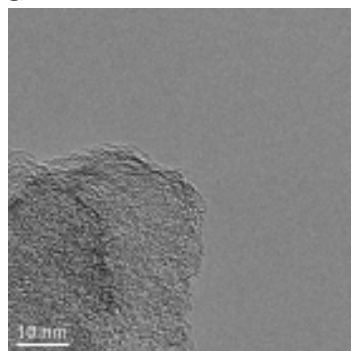


j

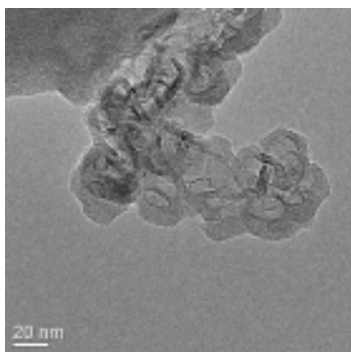
CNF-H4(S=1258m²/g)



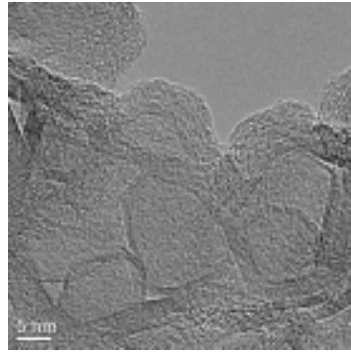
k



l



m



n

CNF-H5(S=1212m²/g)

Fig.4 TEM morphologies of CNF and its activated form

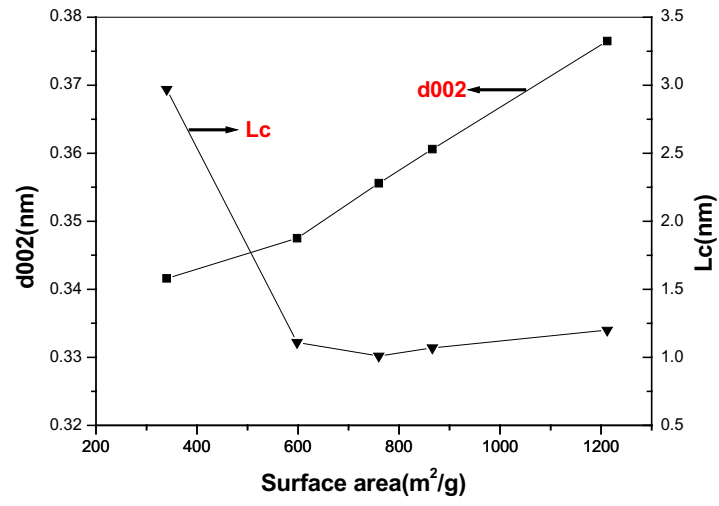


Fig.5 XRD properties of CNF and its activated forms