

CHARACTERIZATION OF ADSORPTION BEHAVIORS OF MOLECULES TO WELL-DEFINED CARBON SURFACES USING SOLID STATE NMR

Yoshinori Matsuo¹, Keiko Ideta², Wei Li¹, Koji Saito³, Jin Miyawaki², Isao Mochida⁴, Seong-Ho Yoon^{1,2*}

¹ Graduate School of Engineering, Kyushu University, Fukuoka 816-8580, Japan.

² Institute for Materials Chemistry and Engineering, Kyushu University, Fukuoka 816-8580, Japan.

³ Environment & Process Technology Center, Nippon Steel Co., Chiba 293-8511, Japan.

⁴ Art, Science and Technology Center for Cooperative Research, Kyushu University, Fukuoka 816-8580, Japan.

*Correspondence author

Introduction

NMR is very powerful for characterizing molecular behaviors on carbon surfaces. We have successfully examined ionic behaviors of electrolytes in supercapacitor through the multi-nuclear solid-state NMR methods [1,2]. Because of various interweaving factors, however, it is not easy to clarify influences of surface properties on the adsorption behaviors of molecules. In this study, we tended to examine the molecular adsorptive behaviors on the special edge and basal surfaces of carbon materials through the solid-state NMR characterization as a fundamental study for molecular adsorption. Special carbon nanofibers (CNFs), platelet-type CNF (PCNF) and tubular-type CNF (TCNF), were selected as basic carbon materials because those are mainly made of edge and basal surfaces.

Experimental

PCNF and TCNF were prepared through the catalytic pyrolysis of mixed gases of C₂H₄ or CO with H₂, respectively. The obtained CNFs were heat-treated at 2800°C in an Ar flow to improve the graphitization degree. The graphitized CNFs (GPCNFs, GTCNFs) were further treated with 30% HNO₃ at 150°C for 24 h to remove dome-like caps formed at edge surfaces by the graphitization process (GPCNF-NA, GTCNF-NA). Finally, GPCNF-NA and GTCNF-NA were heat-treated in H₂/He mixed gas flow at 650°C for 3 h to eliminate oxygen-containing functional groups (H₂-GPCNF-NA, H₂-GTCNF-NA). A preparation scheme of the samples is shown in Figure 1

Scanning electron microscope (SEM) and transmission electron microscope (TEM) were used to confirm the morphologies of the prepared samples. Surface area was calculated by the BET analysis of N₂ adsorption isotherms at 77 K. Oxygen content was determined by CHN analysis.

Surface adsorption property was evaluated by using ²H-NMR (JEOL ECA-400). D₂O and acetone-D₆ were selected as polar molecular probes, and C₆D₆ was used as a non-polar one. CH₃OD and CD₃OH were used to determine preferential adsorption sites within a molecule to the special carbon

surfaces. The spin-lattice relaxation time (T₁) was evaluated to estimate adsorption strengths of the probe molecule with the carbon surfaces.

Results and Discussion

Figure 2 shows TEM images of graphitized, HNO₃-treated, and H₂-treated CNFs. The graphitization process induced the formation of dome-like caps at the graphene edges of the as-prepared CNFs, and thus eliminating imperfect edge structures. The subsequent HNO₃ treatment removed the dome-like caps, and well-aligned graphene edges became exposed as reported previously [3]. Oxygen content increased by the HNO₃ treatment for both CNFs, but the H₂ treatment decreased the oxygen content (data not shown). Compared to HNO₃-GTCNF, the oxygen content of HNO₃-GPCNF having much more exposed edge sites was higher, suggesting the preferential formation of the oxygen-containing functional groups at the edges. The BET surface area of the PCNF series was almost constant (51-53 m²/g) in spite of the post-treatments, whilst an increase of the BET surface area was observed for the TCNF series by the post-treatments (30, 43, and 49 m²/g for GTCNF, GTCNF-NA, and H₂-GTCNF-NA, respectively). Opening of the closed fiber-tips by the HNO₃ treatment could allow N₂ molecules to enter into hollow internal spaces of TCNFs, and the removal the functional groups at hole-edges, which used to prevent the N₂ molecules from entering into the inside, by the subsequent H₂ treatment might give rise to a further increase of accessible surfaces. Appearance of adsorption hysteresis after the HNO₃ treatment supports this hypothesis (data not shown).

The ²H solid-state NMR spectra of D₂O, acetone-D₆, and C₆D₆ on various CNFs with different surfaces are shown in Figure 3. Overall, two different peaks were observed, sharp and broad ones; those peaks could be assigned to non-adsorbed “free” molecule and adsorbed one on the carbon surface, respectively [1,2].

The peaks of adsorbed molecules on GPCNF were observed at lower magnetic field than those of free ones regardless of the polarity of molecules. Non-polar molecules of benzene showed more down field shift as compared to the polar ones of water or acetone. On the contrary, the HNO₃ treatment induced the shift of the peaks of adsorbed molecules to high magnetic field for all molecules used, suggesting that the oxygen-containing functional groups with higher electron density shield the adsorbed molecules from the applied magnetic field, and thus induce the peak shifting to higher magnetic field. The NMR peaks of molecules on H₂-GPCNF-NA were observed at lower magnetic field than those on the GPCNF-NA, maybe because of the removal of the oxygen-containing functional groups by the H₂ treatment. For the TCNF series, the NMR peaks of adsorbed molecules were observed at higher magnetic field than those of the free ones. Similar tendencies were also observed for CH₃OD and CD₃OH (data not shown).

T₁ values are shown in Table 1; the shorter the T₁ value, the stronger the adsorption strength. It was found that the T₁

values were affected by the kinds of the adsorptive molecules and the CNF types. The shorter T_1 values were obtained for the HNO_3 -treated CNFs for all adsorptive molecules, suggesting that the presence of the surface functional groups increases the adsorption strength. Although differences were not remarkable, moreover, the shorter T_1 values for the PCNF series than those for the TCNF series suggest that the edge surface has stronger adsorbing-ability to adsorbed molecules than basal one. Superior adsorption site within a molecule became clear from the T_1 values for CD_3OH and CH_3OD ; the shorter T_1 values for CH_3OD suggest that the polar hydroxyl group is likely to interact strongly with the surface as compared with non-polar methyl group.

Conclusions

From the NMR results using CNFs with the well-defined surfaces, it was confirmed that edge surface has stronger adsorbing-ability to adsorbed molecules than basal surface. Furthermore, surface functionalities were found to increase the adsorption strength with molecules, maybe not only for polar molecules, but also for non-polar ones.

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References

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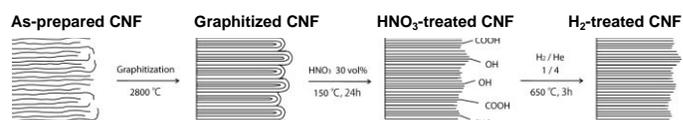


Fig. 1 Schematic illustrations of CNF samples having different surfaces and their preparation scheme.

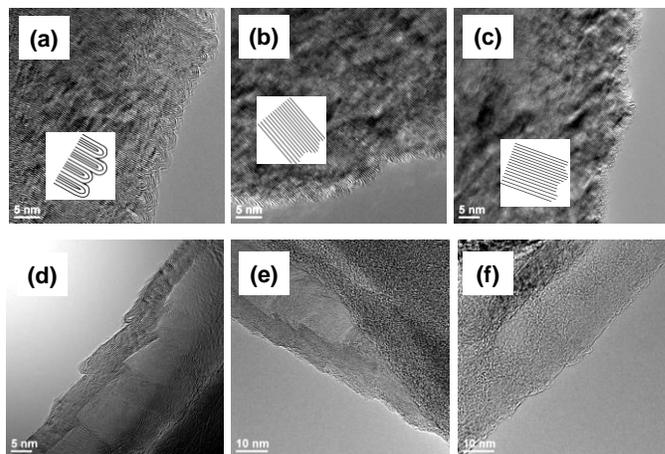


Fig. 2 TEM images of CNFs: (a) GPCNF; (b) GPCNF-NA; (c) H_2 -GPCNF-NA; (d) GTCNF; (e) GTCNF-NA; (f) H_2 -GTCNF-NA.

Table 1. Spin-lattice relaxation time (T_1) of different molecules on various CNFs.

	T_1 (s)					
	GPCNF	GPCNF-NA	H_2 -GPCNF-NA	GTCNF	GTCNF-NA	H_2 -GTCNF-NA
D_2O	1.06	0.52	0.94	2.04	0.98	2.50
acetone- D_6	4.08	3.40	4.50	6.81	4.68	7.88
C_6D_6	1.81	1.08	1.22	1.94	1.57	1.68
CH_3OD	0.49	0.26	1.16	1.37	—	—
CD_3OH	5.54	4.32	5.10	7.57	—	—

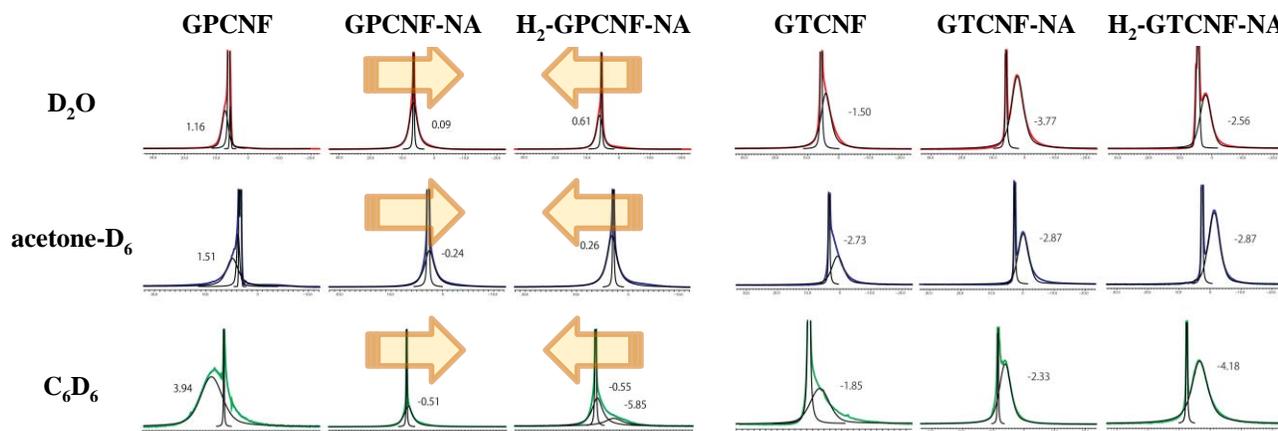


Fig. 3 ^2H solid-state NMR spectra of D_2O , acetone- D_6 , and C_6D_6 on PCNF and TCNF series.