

# INFLUENCE OF SURFACE MODIFICATION OF CUPS-STACKED CARBON NANOTUBES (CSCNTs) ON OXIDATION RESISTANCE

S. Toshinari<sup>1</sup>, K. Chikuba<sup>2</sup> and H. Oda<sup>1</sup>

<sup>1</sup>Department of Chemical Engineering, Kansai University, High Technology Research Center (HRC),  
Kansai University, 3-3-35 Yamate-cho, Suita, Osaka 564-8680, Japan

<sup>2</sup>GSI Creos Corporation, Minami-Watarida-cho, 1-12, Kawasaki-ku, Kawasaki, 210-0855, Japan

## Introduction

Carbon Nanotubes (CNTs) have been vigorously studied for application to various energy storing devices, such as fuel cells, Li-ion batteries, and electrochemical capacitors. However, it has been an important problem recently to improve not only the power generation performance but also the long-term stability and durability. Therefore it is indispensable to clarify the mechanism of the performance degradation with a long-term driving. This degradation seems to be influenced by the corrosion of CNTs used as an electrode material due to the surface state (pore structures and surface functional groups) of CNTs. In this paper, we investigated the surface state of Cups-Stacked Carbon Nanotubes (CSCNTs) with unique structure by determining physical and chemical structural changes of CSCNTs modified by various oxidation treatments (gas-phase oxidation, liquid-phase oxidation, and electrical oxidation). Also, the influence on oxidation resistance of CSCNTs modified by various oxidation treatments was examined by using thermogravimetric analysis (TGA).

## Experimental

### *Preparation of samples*

This study used three types of Cups-stucked carbon nanotubes (CSCNTs), AR10, AR50 and 24PS (tube length; ca.1  $\mu$  m, ca.10  $\mu$  m and ca.20  $\mu$  m, respectively) produced by GSI Creos Corporation, Japan. CSCNTs compose a stacking morphology of truncated conical graphene layers as shown Figure 1. The surface of CSCNTs was modified by the treatments as follows: (1) liquid-phase oxidation in 10% H<sub>2</sub>O<sub>2</sub> for 24h (denoted as LOx); (2) gas-phase oxidation under atmospheric air at 300 K for a retention time of 1 h (GOx); (3) electrical oxidation by applying a voltage of 3 V in 0.1 mol/l HNO<sub>3</sub> for 1 h } (EOx).

### *Characterization method*

Amounts of functional group on the original and modified samples were determined by neutralization titration method. In addition, fractionation of functional groups was studied by using XPS (JEOL, JPS-900MX). The nitrogen adsorption isotherm at 77 K was measured using an automatic gas adsorption apparatus (Belsorp28, BEL JAPAN, INC.). Specific surface area, pore volume, and pore size distribution were analyzed by the B.E.T, DR, and t-plot methods, respectively.

### *Examination of oxidation resistance*

The influence of various surface modification treatments on oxidation resistance of CSCNTs was examined by measuring the combustion onset temperature, using thermogravimetric analysis (Shimadzu TGA-50).

## Results and discussion

Table 1. shows the characteristics of the original and modified CSCNTs. GOx did not change the pore structures of CSCNTs significantly, while both LOx and EOx remarkably decreased micropore volume. Besides, the various oxidation of CSCNT increased the amount of functional groups. LOx could introduce a large number of functional groups. In the present study, functional groups were determined by fractionating into phenolic and carboxyl groups. GOx and LOx could introduce a large number of phenolic hydroxyl groups, while EOx could introduce a large number of carboxyl groups. This result might be consistent with the formation mechanism of the functional group that has been already proposed [1, 2]. That is, a mild oxidation environment such as GOx and LOx might form phenolic hydroxyl groups. In constant, a severe oxidation environment such as EOx might form carboxyl groups.

Additionally, the results of XPS of AR10 shown in Figure 2. and Table 2. gave a similar tendency to the titration method, which could be also seen for AR50 and 24PS.

Figure 3. and 4. show the TGA curves of the original and modified AR10 and 24PS. In general, carboxyl groups are known to be thermally decomposed at a temperature range of 300 to 350°C. The combustion onset temperature of AR10 was ordered as AR10 > AR10-GOx > AR10-EOx > AR10-LOx, which was not consistent with the ranking of functional group as shown in Figure 1. This result might indicate that the difference of the oxidation method changed exposure degree of a lot of open edges that exist on the tube wall of CSCNT, as shown in Figure 5., and that the generation site and the mechanism of the functional group influenced. On the other hand, for 24PS, EOx showed the lowest combustion onset temperature unlike AR10, which might be due to the tube length other than oxidation methods.

## Conclusion

- (1) The functional group could be introduced onto CSCNTs by various oxidation treatments. And it seems that the pore structures and amount of the functional groups can be controlled by selecting the oxidation method.
- (2) Various oxidation treatments influenced the oxidation resistance of CSCNTs from the appearance of the difference to the combustion onset temperature.

Therefore, the chemical structure of CSCNT can be optimized, and the application to the material for the energy device can be expected.

## References

- [1] M.Nakahara and Y.Sanada, 1995. Characterization and modification of carbon material surface TANSO 167: 116-124. (in Japanese)
- [2] Z.R.Yue, W. Jiang, L. Wang, S.D. Gardner and C.U.Pittman, Jr. 1999. Surface characterization of electrochemically oxidized carbon fibers Carbon 37: 1785-1796.

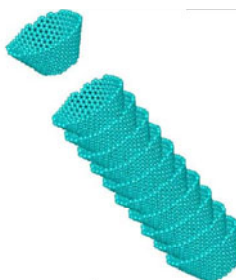


Figure 1. Structure model of CSCNT.

Table 1. Characteristics of samples used.

Samples	$S_{BET}$ [ $m^2/g$ ]	$V_{micro}$ [ml/g]	$V_{meso}$ [ml/g]	Total acidity [mmol/g]	COOH [mmol/g]	OH [mmol/g]
AR10	64	0.0036	0.189	0.47	0.06	0.40
AR10-GOx	59	0.0018	0.198	0.72	0.25	0.47
AR10-LOx	59	0.0009	0.160	4.11	0.03	4.08
AR10-EOx	60	0.0005	0.224	0.69	0.39	0.30
AR50	45	0.0101	0.115	0.40	0.15	0.26
AR50-GOx	45	0.0080	0.141	0.35	0.13	0.23
AR50-LOx	31	0.0011	0.080	2.41	0.74	1.67
AR50-EOx	42	0.0041	0.117	0.54	0.31	0.22
24PS	47	0.0077	0.135	0.41	0	0.41
24PS-GOx	46	0.0064	0.133	0.53	0.11	0.43
24PS-LOx	38	0.0011	0.124	1.15	0.64	0.51
24PS-EOx	27	0	0.132	0.93	0.52	0.41

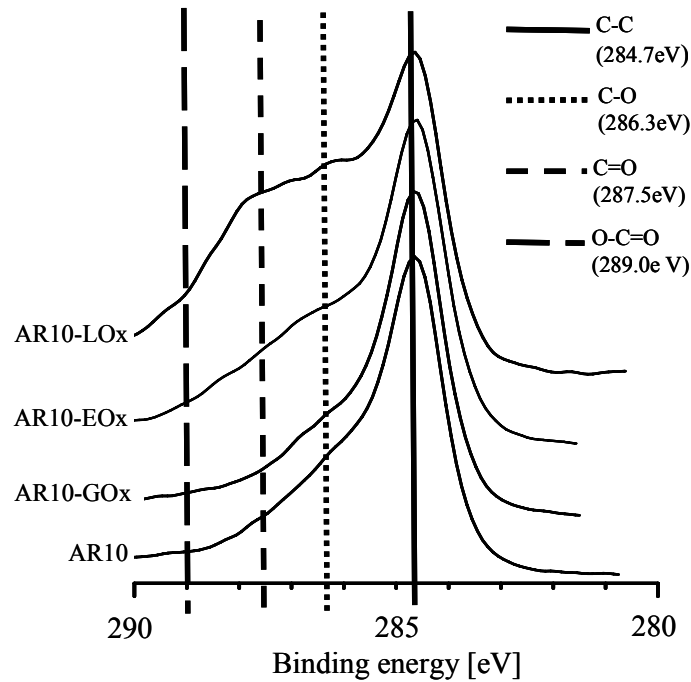


Figure 2. Photoelectron lines of C1s in modified AR10.

Table 2. XPS analysis of C1s spectra of modified AR10.

Samples	C-C (284.7eV)	C-O (286.3eV)	C=O (287.5eV)	O-C=O (289.0eV)
AR10	100	33.5	15.1	10.8
AR10-GOx	100	35.5	4.8	18.7
AR10-LOx	100	16.3	20.4	13.7
AR10-EOx	100	39.9	25.4	32.7

X-ray source: MgKv1

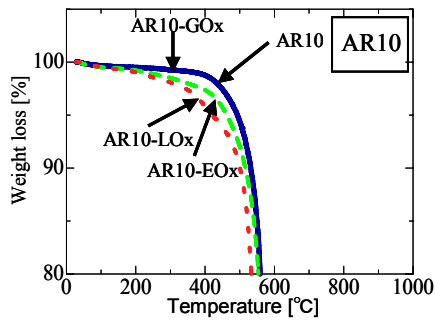


Figure 3. Thermogravitics analysis of modified AR10.

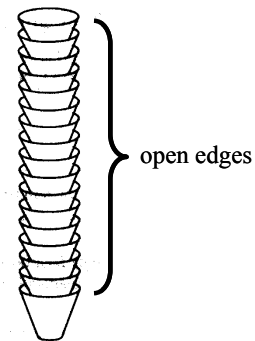


Figure 5. Structure model of open edges at the outer surface of CSCNT.

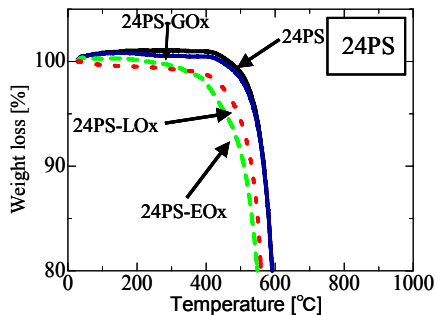


Figure 4. Thermogravitics analysis of modified 24PS.