

## 불소처리 온도가 탄소나노튜브의 표면특성에 미치는 영향

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### Influence of Fluorination Temperature on Surface Characteristics of Carbon Nanotubes

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#### 1. Introduction

Since the discovery of single-wall carbon nanotubes (SWNTs) there has been a flurry of research activity aimed at understanding their physical properties, elucidating their growth mechanisms and developing novel uses for them. Chemistry involving SWNTs is still in its infancy. This is due, in large part, to previous difficulties in obtaining reasonable quantities of highly purified SWNTs[1].

In contrast to the open tube ends, the side-walls of the SWNTs, by virtue of their aromatic nature, possess a chemical stability akin to that of the basal plane of graphite. The chemistry available for modification of the nanotube side-wall is thus significantly more restrictive.

In this work, using technology developed in the fluorination of carbon fibers, we investigate on the physicochemical manipulation of the SWNT side-wall by direct fluorinating high-purity SWNTs.

#### 2. Experimental

##### 2.1. Materials and fluorination procedure

The single-walled carbon nanotubes (SWNTs) studied in this work were manufactured by CVD process (CVD SWNT, supplied from ILJIN Nanotech of Korea, degree of purity is >95 wt%, length: 10~50  $\mu\text{m}$ , diameter: 10~20 nm). The  $\text{F}_2$  and  $\text{N}_2$  gases used were 99.99 + % pure.

SWNTs were subjected to fluorination in different conditions. The fluorination reaction was performed in a batch reactor made of nickel with an outer electric furnace. After evacuation, fluorine ( $\text{F}_2$ ) was introduced to the reactor at room temperature, and then the reactor was heated to the treatment temperature. The fluorine pressure was 1 MPa and the nominal reaction time was 1 h at the treatment temperature.

##### 2.2. Measurements

Raman spectroscopy (Jobin yvon, S320C) was used for the carbon properties (the strength of G-band and the  $I_d/I_g$  ratio). Changes in the surface morphology of fluorinated SWNTs were examined using scanning electron micrographs (SEM, JEOL JSM-840A).

### 3. Results and Discussion

Fig. 1 shows the Raman spectrum of the pure, untreated SWNT material. The smaller peak at  $186\text{ cm}^{-1}$  is due to a characteristic breathing mode of the SWNTs. Raman spectra of SWNTs fluorinated for 1 h at reaction temperatures of 100, 300, and  $400^\circ\text{C}$  are also shown in Fig. 1. Trace (a), corresponding to the reaction at  $300^\circ\text{C}$ , shows only two broad peaks centered around 1340 and  $1580\text{ cm}^{-1}$  and a broad band fluorescence. The Raman peaks correspond to  $\text{sp}^3$  and  $\text{sp}^2$  carbon stretching modes, respectively. At higher reaction temperatures, yielding high F to C ratios, these peaks disappear and the fluorescence is attenuated. As C-F bonds are not very polarizable, it is understandable that they are not seen in the Raman spectra presented here.

Fig. 2 shows the purified starting material and the same materials after fluorination at  $300^\circ\text{C}$  for 1 h. The image shows excessive charging due to its insulating nature, but the rope-like structure of tubes is still evident.

Consequently, Raman spectroscopy confirm the formation of new chemical and physical bonds to the nanotube superstructure[2]. Contributions of adsorbed molecular fluorine to the overall fluorine uptake are precluded at these temperatures. Therefore, we have demonstrated that large amounts of fluorine is being physically attached to the side-wall of the SWNTs.

### 4. References

- 1) S. Iijima and T. Ichihashi, *Nature*, **363**, 603(1993).
- 2) S. J. Park, M. K. Seo, and Y. S. Lee, *Carbon*, In press.

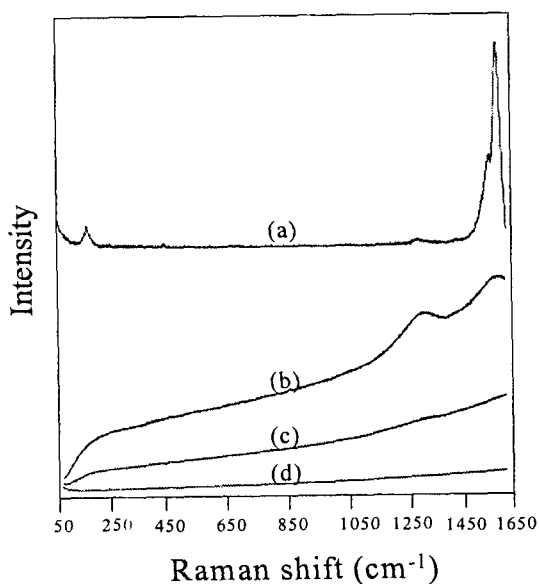


Fig. 1. Raman spectrum of pure and fluorinated SWNTs: (a) untreated, (b)  $100^\circ\text{C}$ , (c)  $300^\circ\text{C}$ , (d)  $400^\circ\text{C}$ .

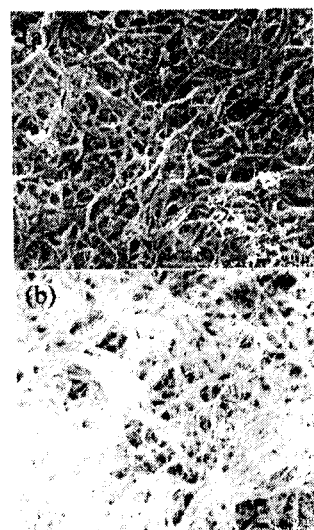


Fig. 2. SEM pictures of untreated and fluorinated SWNTs: (a) untreated and (b) fluorinated at  $300^\circ\text{C}$ .