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Chemical Modification of Multi-walled Carbon Nanotubes (MWNTs) By Vacuum Ultraviolet (VUV) Irradiation Dry Process

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1. Introduction

Carbon nanotubes (CNTs) [1] have been intensively investigated due to not only their unique atomic arrangement but also very interesting physical properties as well [2]. Possible applications of CNTs include nanoelectronics, such as field-effect transistors, single-electron transistors/sensors [3], and LSI interconnection [4]. The controlled modification or functionalization of the sidewalls of CNTs is one of the most fundamental technologies for these device applications. There are few reports about the dry process for chemical modification, although a dry process is more advantageous than a wet process from many points of view: throughput, yield and cost. Mawhinney [5,6] and Cai [7] reported that the oxidation of single-walled carbon nanotubes (SWNTs) in a O_3 or UV/O_3 gas-solid interface reaction produced a series of oxygenated groups. However, they did not measure the amount of functional groups, quantitatively.

In this paper, we report for the first time a very high-speed dry process for chemical modification of multi-walled carbon nanotubes (MWNTs) using VUV oxidation and X-ray photolelectron spectroscopy (XPS) measurements for determining the amount of functional groups and the speed of this process.

2. Experiments

CVD growth of MWNTs

Vertically aligned MWNTs were grown using hot filament CVD at 540°C in a low-pressure chamber [8]. A 30 nm Ni film was used as a metal catalyst, being deposited on a 50 nm Ti film on a Si substrate. The average length and outer diameter of MWNTs are about 1.0 μm and 10-15 nm, respectively. The MWNTs were cleaned by annealing for 40 min at 400°C in the air for removing chemically active impurities such as low-molecular weight amorphous carbon.

Chemical modification of MWNTs

An excimer UV light generator (Xe gas sealed) was used. The MWNTs on the substrate were exposed by VUV (λ=172 nm) under atmospheric pressure in 1% O_2 gas (diluted air by N_2). The chemical oxidation feature was analyzed by ATR (Attenuated Total Reflection) FT-IR, and XPS. The MWNTs and ferritin molecules (which can be observed with TEM) were covalently bonded in aqueous solution including NHS 0.25 mol/l and EDC 0.25 mol/l for 24hrs at room temperature.

3. Results and discussions

Figure 1 shows the ATR FT-IR spectrum of the MWNT sample at VUV irradiation time of 6 min. The absorption of carboxyl (-COOH), quinone, and ester (-COOR) groups can be assigned to the band of 1710, 1660 and 1725 cm^{-1}, respectively. This suggests that the VUV-dry oxidation process has introduced a large amount of oxygenated groups, while keeping the primary CNT graphene sheet structure.

We measured the integrated intensity of each component of carbon 1s spectra (XPS) of the modified MWNTs. Figure 2 shows the amount of oxygenated groups in atomic% at different reaction times. Note that most of carboxyl groups were formed in one minute and the total amount of the groups is about 3 atomic% of all C-C bonds in the MWNTs. The high-speed oxidation may be attributable to the generation of a large amount of O_2 singlet and/or hydroxyl radicals by the VUV irradiation.

Figures 3 show TEM and EDX images of the modified MWNTs. In order to confirm the introduction of carboxyl groups, ferritin molecules were covalently bonded with the carboxyl group. As you can see clearly, the iron core of ferritin molecules are observed only on the tube with the carboxyl group.

3. Conclusions

We have demonstrated a high speed and dry process for chemical modification of multi-walled carbon nanotubes (MWNTs) using VUV/O_3 oxidation. From the XPS spectra, we confirmed that carboxyl (-COOH) groups of 3 atomic% were formed on the sidewalls of MWNTs within one minute reaction. We believe that this kind of dry process for carbon nanotube devices will become more and more important in the real applications in the future.

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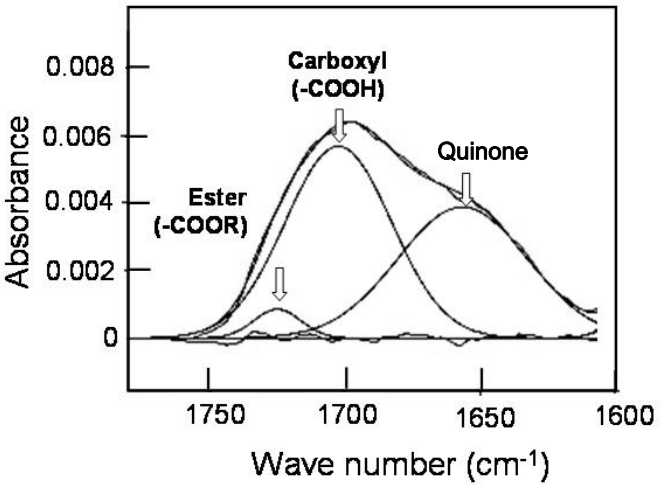


Figure 1 ATR FT-IR Normalized Spectrum of VUV exposed MWNTs

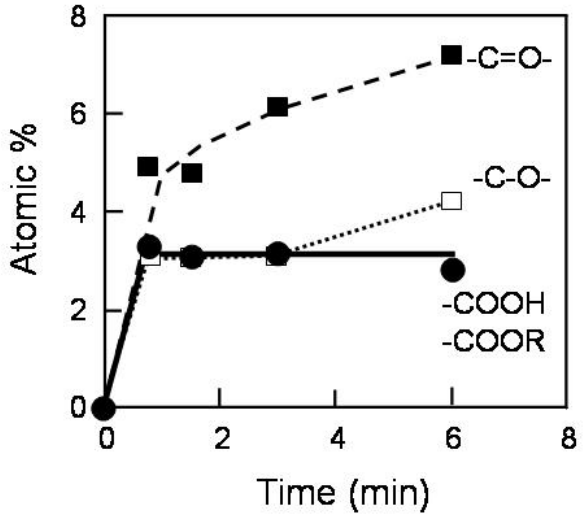
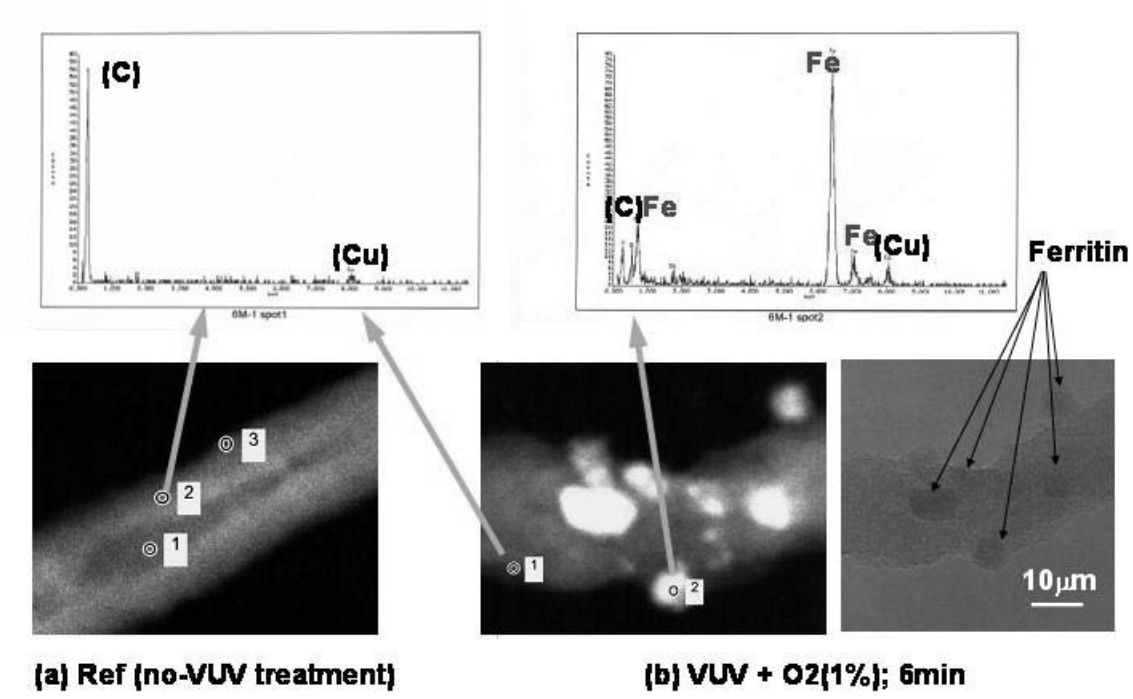


Figure 2 The amount of oxygenated groups in atomic% at different reaction times obtained by XPS



Figures 3 TEM and EDX images of (a) non-VUV treatment and (b) modified MWNTs.