Etching Effects of Ultraviolet Irradiation on Multiwalled Carbon Nanotubes

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The relationship between the activation energy, crystallinity, and morphology of UV-irradiated multi-walled carbon nanotubes (MWCNTs) was systematically investigated. Using total UV energy as an index, MWCNTs were irradiated with ultraviolet light at 254 nm and 185 nm. The activation energy of the MWCNTs was 320 kJ/mol prior to irradiation and 154 kJ/mol after irradiation with 16174 J/cm² of total UV energy. In addition, the value of the I_G/I_D ratio for the MWCNTs was 7.12 prior to irradiation and 3.63 after irradiation with 16174 J/cm² of total UV energy. Transmission electron microscopy (TEM) observations showed that the outer layers of the MWCNTs were increasingly etched away and the linearity of the graphite layer was lost as the total UV energy increased. In addition, when the total UV energy exceeded 10856 J/cm², the hollow structure of the MWCNTs was completely lost. It was therefore found that, as the energy of the incident ultraviolet light increases, the activation energy of MWCNTs decreases, the crystallinity deteriorates, and the morphology changes. Furthermore, it was demonstrated that the level of total UV energy exposure can be used as an indicator of the morphology, activation energy, and crystallinity of UV-irradiated MWCNTs.

Keywords: UV Intensity, Total UV Energy, Activation Energy, Thermogravimetry-Differential Thermal Analysis, Transmission Electron Microscopy, Raman Spectroscopy

1. Introduction

Since carbon nanotubes (CNTs) were first discovered by Iijima, their study has significantly advanced, because CNTs have excellent mechanical and electrical properties, and can be applied in numerous fields. In many cases, prior to use, surface oxidation of CNTs is required; thus, this process has been the subject of many studies. Methods for CNT surface oxidation include liquid phase methods, vapor phase methods, and simpler and easier UV irradiation methods.

There have been reports on the morphology of multi-walled carbon nanotubes (MWCNTs) prepared using the vapor phase, liquid phase, and UV irradiation methods. In addition, we previously reported on the morphology of MWCNTs produced using a combination of hydrogen peroxide water and UV irradiation, and UV irradiation alone.

While UV irradiation has been shown to be effective for surface oxidation of MWCNTs, the morphology of the body of a single MWCNT due to oxidation has not yet been systematically studied or reported. In addition, because different studies on the effect of UV irradiation on MWCNTs have involved the use of different types of UV irradiation equipment and irradiation times, there is no basic information available on the effect of UV irradiation on the morphology of the body of a single MWCNT.

The main purpose of this study, therefore, was to systematically clarify the influence of surface oxidation via UV irradiation on the morphology of MWCNTs. Furthermore, using the total UV energy as an index independent of the specific UV irradiation equipment and irradiation time, the relationship between the activation energy, crystallinity, and morphology of UV-irradiated MWCNTs was investigated.

2. Experimental Section

The MWCNTs used in this study were vapor-grown carbon fibers (VGCFs; Showa Denko K.K.). Ten sets of vials (SV-20; Nichidenrika-Glass Co., Ltd.) were prepared, each containing 4 mg of MWCNTs.

Fig. 1 schematically shows the vertical and horizontal sections of the UV irradiation equipment used in the study. The external form was a rectangular parallelepiped (95 mm × 95 mm × 300 mm) constructed of 2-mm-thick paper board. Four 6-W ozone lamps (GL6ZH; Sankyo Denki Co., Ltd.) were placed in parallel in the upper portion. The ozone lamps emitted UV radiation at 254 nm and 185 nm. To maintain the equipment at room temperature during irradiation, 92 mm cooling fans (OWL-FY0925L; Owtech Corp.) were placed in front of and behind the equipment.

To determine the total UV energy received by the vials, the UV irradiation equipment was first operated for 24 hours and then the UV intensity was measured at a wavelength of 254 nm using a UV illuminometer (UV-M03A; Oak Manufacturing Co., Ltd.) at the position of the vials. The total UV energy was then calculated.

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Nine vials containing MWCNTs were placed in the position of MWCNTs, simultaneous thermogravimetry (TG)-differential thermal analysis (TG-DTA) was performed using an EXSTAR TG/DTA6200 (platinum cup; Hitachi High-Tech Science Corp.) for both the non-irradiated MWCNTs and the MWCNTs sampled at a rate of one vial per 120 h after initiation of UV irradiation. Note that for all of these measurements, the temperature was raised at a rate of 10 °C/min in pure air (200 ml/min), and the measured mass was normalized to 100, which corresponded to a reference sample dried for 15 min at 130 °C. In addition, Raman spectroscopy analyses of the MWCNTs were performed using an NRS-3200 (green laser; excitation wavelength 532 nm; JASCO Corp.), and the morphology of the MWCNTs was evaluated via transmission electron microscopy (TEM) using an H-9500 (acceleration voltage 200 kV; Hitachi High-Technologies Corp.).

### 3. Results and Discussion

Table 1 lists the intensity at 254 nm, the irradiation time, and the total UV energy for each vial position. The total UV energy that each UV-irradiated MWCNTs sample was exposed to was determined using the data in Table 1.

First, the weight change due to oxidation of the MWCNTs as a result of UV-irradiation was investigated. Fig. 2 presents the TGA curves for the non-irradiated MWCNTs and the MWCNTs irradiated with different total UV energies. For the non-irradiated MWCNTs, oxidation began at approximately 742 °C and was completed at approximately 855 °C. In contrast, for the MWCNTs irradiated with a total of 16174 J/cm² of UV energy, oxidation began at approximately 508 °C and was complete at approximately 816 °C. These results indicated that the initial temperature for oxidation of the MWCNTs decreased as the amount of total UV energy increased.

Weight loss analysis was then performed using the method proposed in reference 19. The weight loss due to oxidation of the MWCNTs is given by:

\[
\Delta m/m_0 = k t \quad \text{…………………………..(1)}
\]

where \(m_0\) is the initial weight of the MWCNTs, \(\Delta m\) is the weight loss of the MWCNTs at time \(t\), and \(k\) is the reaction rate constant, which does not change if the temperature is constant, for non-isothermal measurements. In addition, the differential coefficient \(d(\Delta m/m_0)/dt\) over the time interval \(t \rightarrow t'\) is considered to be equal to the reaction rate constant \(k\) at the temperature corresponding to the time \(t'\), and thus is given by:

\[
k = d(\Delta m/m_0)/dt \quad \text{…………………………..(2)}
\]

from Eq. (1). In addition, the temperature dependence of the reaction rate constant is expressed using the Arrhenius equation:

\[
\ln k = \ln A - (Ea/R)/T \quad \text{…………………………..(3)}
\]

where \(A\) is the pre-exponential factor, \(Ea\) is the activation energy (kJ/mol) for the MWCNTs, \(R\) is the universal gas constant (J/mol·K⁻¹), and \(T\) is the absolute temperature (K). From Eqs. (2) and (3), we then have:

\[
\ln [d(\Delta m/m_0)/dt] = \ln A - (Ea/R)/T \quad \text{…………………………..(4)}
\]

In this case, because the temperature change is nearly zero, \(A\) is eventually constant over time \(t \rightarrow t'\), and as a result the Arrhenius curve plots the relationship between \(\ln [d(\Delta m/m_0)/dt]\) and \(1/T\) for the entire oxidation process. The activation energy is obtained from the slope of this curve. Fig. 3 shows the Arrhenius plots for the non-irradiated MWCNTs and the MWCNTs irradiated with different total UV energies calculated from the corresponding TGA curves (Fig. 2), and it can be seen that the Arrhenius curves are linear. The activation energies obtained from the Arrhenius curves are shown in Fig. 5. The activation energy for the non-irradiated MWCNTs was 320 kJ/mol, while the activation energy for the MWCNTs irradiated with a total UV energy of 16174 J/cm² was 154 kJ/mol. This result indicated that the activation energy for the MWCNTs decreased as the exposure to total UV energy increased.

The Raman spectra of the UV-irradiated MWCNTs were then evaluated. Fig. 4 presents the Raman spectra of the non-irradiated MWCNTs and the MWCNTs irradiated with different total UV energies. The peak near 1580 cm⁻¹ is referred to as...
the G band and is due to the in-plane stretching vibration of the six-membered carbon ring structure in graphite. The peak near 1350 cm$^{-1}$ is referred to as the D band and is due to defect structures. It is known that the intensity of the D band increases following irradiation with total UV energy, and the observed ratio of the intensities of the G and D bands ($I_G/I_D$) is used as an indication of the crystallinity of MWCNTs\(^{19,22}\). \textbf{Fig. 5} presents the $I_G/I_D$ ratios for the peaks in the spectra shown in \textbf{Fig. 4}. Notably, the $I_G/I_D$ ratio was 7.12 prior to UV irradiation and declined to a value of 3.63 after irradiation with UV energy totaling 16174 J/cm\(^2\), indicating that the crystallinity of the MWCNTs deteriorated as the amount of total UV energy increased.

Finally, the morphology of the UV-irradiated MWCNTs was investigated. A TEM image of the non-irradiated MWCNTs is shown in \textbf{Fig. 5(A)}, and it can be seen that the surface of the MWCNTs was relatively smooth. \textbf{Fig. 5(B-J)} present TEM images of the MWCNTs irradiated with different total UV energies. It can be seen that in \textbf{Fig. 5(B)}, the surface of the MWCNTs was scarcely changed and the morphology was close to that of the non-irradiated MWCNTs. Therefore, below 691 J/cm\(^2\) of total UV energy, oxygen functionality can be introduced into the surface of the MWCNTs without degrading their morphology\(^{12}\). On the other hand, the surface structure of the MWCNTs was coarse in \textbf{Fig. 5(C-F)}, indicating that the UV-MWCNTs reaction...
began to occur from the outer surface and then occurred inward. In addition, an increasing number of graphite layers were etched away as the total UV energy increased, and the linearity of the structure was lost. For total UV energies of 1494 J/cm² to 6696 J/cm², modification of the morphology of the MWCNTs and introduction of oxygen functionality thus occurred in parallel. Therefore, using this method, it should be possible to increase the platinum loading or amount of catalyst carrier material in fuel cells without increasing the quantity of MWCNTs\(^{15}\).

In addition, after exposure to 8994 J/cm² of total UV energy, the tip of the MWCNTs was sharp and had a relatively large diameter, as shown in Fig. 5(G). MWCNTs with a similar morphology have been obtained after etching MWCNTs with ethanol gas\(^{20}\). Therefore, it should be possible to construct probes for scanning probe microscopy by exposing MWCNTs to a total UV energy level of 8994 J/cm². It should also be noted that there were only a few MWCNTs lacking a hollow structure at this energy level, while there were many MWCNTs lacking a hollow structure (Fig. 5(H–J)) after irradiation with higher total levels of UV energy, likely due to degradation of the graphite or graphene that constitutes the hollow structure of MWCNTs. As a result, after exposure of the MWCNTs to high total levels of UV energy, their morphology resembled that of graphene nanoribbons obtained after oxidation of MWCNTs using a mixture of potassium permanganate and sulfuric acid\(^{15}\). Thus, at total UV energies greater than 10856 J/cm², graphene nanoribbons can be generated from MWCNTs.

Ultraviolet light with wavelengths of 185 nm and 254 nm has approximately 647 kJ/mol and 472 kJ/mol of energy, respectively\(^{20}\). It can be seen in Fig. 5 that the non-irradiated MWCNTs exhibited activation energy of 320 kJ/mol. Therefore, exposure to ultraviolet light at either wavelength leads to breakage of the chemical bonds of MWCNTs. However, Sugimura negated the validity of simply comparing the UV energy and chemical bond energy with respect to the breakage of chemical bonds\(^{20}\). When atmospheric oxygen (O\(_2\)) is irradiated with 185 nm UV light, the oxygen is converted to ozone (O\(_3\)). On the other hand, when atmospheric oxygen (O\(_2\)) is irradiated with 254 nm ultraviolet light, ozone (O\(_3\)) is decomposed. During the generation and decomposition of O\(_3\), atomic oxygen, which is highly reactive, is generated\(^{20-21}\). In the present study, both the oxidation of MWCNTs by atomic oxygen and the introduction of oxygen functionality increased as the total UV energy increased; as a result, the morphology of the MWCNTs changed, the activation energy of the MWCNTs decreased, and the crystallinity was degraded.

Furthermore, the use of the total exposure to UV energy, rather than the wavelength of UV light, was found to be useful for comparing previously reported results regarding the surface oxidation of MWCNTs\(^{12-15}\), because the UV energy is a useful index for predicting the morphology of MWCNTs that is independent of the wavelength of UV light. A UV source with two wavelengths—254 nm and 185 nm—was used in this study, while other studies have reported the use of UV sources with different wavelengths\(^{20,15}\). It can also be expected that future evaluations will require the use of UV sources with different wavelengths.

These results systematically clarified the relationship between the surface oxidation of UV-irradiated MWCNTs and the changes in the morphology of the body of a single MWCNT due to irradiation. In addition, it was shown that the total UV energy used to irradiate MWCNTs serves as a good indicator of the morphology, activation energy, and crystallinity of UV-irradiated MWCNTs.

### 4. Conclusions

Using the total UV energy as an index, the following conclusions were obtained for UV-irradiated MWCNTs:

1. The activation energy was 320 kJ/mol for non-irradiated MWCNTs and 154 kJ/mol for MWCNTs irradiated with a total UV energy of 16174 J/cm². It was also confirmed that the activation energy of MWCNTs decreases as the total UV energy increases.

2. The \(I_d/I_0\) ratio was 7.12 for the non-irradiated MWCNTs and 3.63 for the MWCNTs irradiated with a total UV energy of 16174 J/cm². It was also confirmed that the crystallinity of MWCNTs deteriorates as the total UV energy increases.

3. The morphology of the surface of the non-irradiated MWCNTs was relatively smooth as observed using TEM; however, when the total UV energy was increased, etching of the outer layer of the MWCNTs occurred and the linearity of the graphite layer was lost. In addition, when the total UV energy exceeded 10856 J/cm², the hollow structure was decomposed in many of the MWCNTs. Therefore, it was confirmed that the morphology of MWCNTs changes significantly as the total UV energy increases.

On the basis of the above results, the morphology of UV-irradiated MWCNTs was systematically clarified. In addition, it was shown that the total UV energy is a good index for discussing the morphology, activation energy, and crystallinity of UV-irradiated MWCNTs.

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