pH dependence of water-solubility of single-walled carbon nanotubes treated by microplasma in aqueous solution

K. Imasaka, U. Khaled, S. Wei, J. Suehiro

Graduate School of Information Science and Electrical Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395 Japan

Abstract: Single-walled carbon nanotubes (SWCNTs) were solubilized by microplasma in pH-controlled aqueous solution. The SWCNTs were highly dispersed and solubilized in water under higher pH condition (pH > 9). Surface of the SWCNT was functionalized by carboxylate ion (-COO⁻) and negatively charged during the microplasma treatment. A possible mechanism of water-solubility of SWCNT was briefly discussed.

Keywords: pH, microplasma, water-solubility, carbon nanotube, aqueous solution

1. Introduction

Carbon nanotubes (CNTs) have unique electrical, mechanical and chemical properties. However, a drawback to their applications is poor solubility in water or organic solvents. Thus far, several approaches have been attempted to solubilize CNTs, such as covalent or noncovalent functionalization [1], chemical oxidation [2], addition of surfactants [3], polymer wrapping [4]. We have previously proposed a novel technique of water-solubilization of multi-walled CNTs (MWCNTs) and single-walled CNTs (SWCNTs) based on a microplasma treatment in water [5-7]. This method has a distinctive advantage in that it does not need any particular chemical agents or additives for CNT solubilization.

The microplasma generated in aqueous solution, which can produce various active chemical species such as OH⁻ (hydroxyl), O²-, H²O₂, HO₂, and O₃ (ozone), has attracted much attention as a new chemical reaction scheme for various applications such as sterilization and removal of organic pollutants and bacteria [8]. Our previous studies [5-7] were the first attempts to utilize these active radicals for the modification of nanomaterial properties. It is well known that electrical discharge phenomena in aqueous solution are remarkably affected by the solution conductivity and pH [9,10]. These previous studies, which investigated effects of pH and conductivity of the aqueous solution on the electrical discharge and resultant radical formation and chemical reactions, motivated us to investigate their effects on CNT solubilization process using microplasma in water.

In this study, SWCNTs were treated by the microplasma in aqueous solutions with different pH and influence of pH condition on SWCNT solubility was investigated based on the results of optical emission spectra from the microplasma, Fourier transform infrared (FTIR), x-ray photoelectron spectroscopy (XPS), Raman spectroscopy analysis and zeta potential measurement of the microplasma-treated SWCNTs.

2. Experimental procedure

A schematic diagram of the experimental setup for SWCNT solubilization using microplasma in water is shown in Fig. 1. The microplasma (pulsed streamer discharge) was generated between a tungsten wire and stainless steel plane electrode, which were installed in a rectangular acrylic chamber filled with the SWCNT suspension of 100mL. The SWCNTs were suspended in deionized water at concentration of 0.1 mg/mL. The pH of the SWCNT suspension was adjusted to acidic condition (pH ≈ 3) by adding H₂SO₄ or HNO₃, and to basic condition (pH ≈ 10) by adding KOH or NH₃. Regardless of pH, electrical conductivity of SWCNT suspension was almost constant same value except for a control sample (pure deionized water, pH ≈ 7) so that possible influences of
Fig. 2 Photographs and Normalized UV-visible absorbance of SWCNT suspension treated by the microplasma under different initial pH condition.

Pulsed high voltage output (500 ns pulsed width, 80 kV peak voltage and 25 Hz repetition rate) was generated by using a homemade pulsed power generator based on a Blumlein transmission line. The output voltage was applied to the wire electrode. The gap length between the wire and the plane was 25 mm. During the microplasma treatment for 1 h, the SWCNT suspension was gently stirred by a magnetic stirrer to prevent the SWCNTs from precipitating at the bottom of the chamber.

3. Results and discussion

3.1 Water-solubility of microplasma treated SWCNTs

Fig. 2 shows photographs and UV-visible absorbance of SWCNT suspensions after the microplasma treatment under different pH conditions. The UV-visible absorbance of SWCNT suspensions was measured for quantitative evaluation of SWCNTs solubility. A typical UV-visible absorption spectrum of SWCNT suspension under basic condition was depicted in Fig. 2 and an absorption peak was noticed at 256 nm wavelength. Similar spectra were also obtained under different pH conditions. The absorbance peaks under acidic and basic condition were normalized by that obtained under neutral condition. It was found from the photographs in Fig. 2 that after the microplasma treatment under acidic condition (pH ≈ 3), the SWCNTs were aggregated and precipitated. On contrary, the SWCNTs treated by the microplasma under neutral (pH ≈ 7) or basic condition (pH ≈ 10) were well dispersed and solubilized. Comparing the microplasma-treated SWCNT suspensions under neutral and basic condition by just only eye observation, solubility of SWCNTs looks like almost same each other. However, the normalized absorbance clearly revealed that the absorbance under basic condition adjusted to pH ≈ 10 by KOH and NH$_3$ was increased more than two times compared to that under neutral condition, while the absorbance was considerably decreased under acidic condition adjusted to pH ≈ 3 by H$_2$SO$_4$ and HNO$_3$.

3.2 Surface analysis of SWCNTs

It has been experimentally found that the water solubility of the microplasma-treated SWCNT could be improved by adjusting the initial pH to basic range. In order to investigate a mechanism of pH dependency of water-solubility of SWCNT, surface of the SWCNTs was analyzed using FT-IR and XPS measurements.

Fig. 3 shows FTIR absorption spectra of the SWCNTs treated by microplasma in deionized water (neutral), H$_2$SO$_4$ (acid) and KOH (basic) solution. Surface of the vacuum-dried SWCNTs was analyzed using KBr-pellet method of FTIR measurement. After the microplasma treatment, two absorption band peaks were newly detected at 1380 and 1580 cm$^{-1}$ for all SWCNTs regardless of the pH value. These two absorption band peaks are assigned to carboxylate ion (-COO$^-$) groups, which are originated from -COOH groups.

Chemical compositions of SWCNT surface were further analyzed in detail by XPS measurement. Fig. 4 shows XPS wide-scan spectra of the SWCNT powder before and after the microplasma treatment under various pH conditions. A major peak of carbon (C1s) and a minor peak of oxygen (O1s) were detected before the microplasma treatment. The XPS analysis revealed that the microplasma treatment increased the atomic percentage concentration of O1s from 23 to 43 %, 51 and 48 % under
Fig. 4 XPS wide scan spectra of SWCNT before and after the microplasma treatment under different pH condition.

Fig. 5 Raman spectra of SWCNT before and after the microplasma treatment under different pH condition.

acidic, neutral and basic conditions, respectively. The results of FTIR and XPS measurements suggest that the SWCNT surface was functionalized with -COO\(^{-}\) groups, which could be introduced by chemical reactions between SWCNT surface and strong oxidant such as O\(^{\cdot}\) radicals and O\(_3\) generated by the microplasma treatment regardless of the pH value.

In conventional solubilization methods of SWCNT using acid treatment, the SWCNT surface was intentionally damaged by the chemical oxidation in order to enhance chemical groups introduction to open ends or the defect sites on the sidewall. It is interesting to examine if the SWCNT surface is damaged also by the microplasma treatment depending on the pH value. Fig. 5 compares Raman spectra of SWCNT powders before and after the microplasma treatment. Two main peaks at the G band (1590 cm\(^{-1}\)) and D band (1350 cm\(^{-1}\)) were observed. It is known that the G band is attributed to graphite-like materials with a high crystallinity, while the D band corresponds to amorphous carbon or defects with a lower crystallinity. The spectral ratios of the D band to the G band before and after the microplasma treatment were almost same and pH dependence was not clearly observed. This result implies that -COO\(^{-}\) groups terminate initial defects on the SWCNT surface, which were generated during the SWCNT production.

In the previous section, it was revealed that microplasma-treated SWCNTs were functionalized with -COO\(^{-}\) groups without depending initial pH conditions. The -COO\(^{-}\) groups could give negative electric charge to SWCNT surface, and would improve water dispersibility of SWCNTs due to their electrostatic repulsion force between them [11-13]. In order to quantify electric charge on SWCNT surface, zeta potential of the SWCNTs treated by the microplasma under different initial pH conditions was measured.

Fig. 6 shows pH dependence of zeta potential of SWCNTs treated by microplasma. The pH values in Fig. 6 correspond to those measured after the microplasma treatment, which slightly decreased from the initial value. Zeta potential of SWCNTs treated by the microplasma under acidic condition (H\(_2\)SO\(_4\) and HNO\(_3\)) was -12.5 mV, which was almost equal to that of SWCNTs measured in deionized water before the microplasma treatment. On the other hand, zeta potential of microplasma-treated SWCNTs significantly decreased with higher pH values under neutral and basic conditions. The zeta potentials of SWCNTs in deionized water, KOH and NH\(_3\) solution were -30, -40, and -46 mV, respectively. The lowest zeta potential was -46 mV, which was obtained with basic solution adjusted by NH\(_3\) (pH \(\approx\) 9) and was almost equal to that measured with CNTs treated by SDS [3] or concentrated acid [14, 15] for higher water solubility.

3.3 Mechanism of pH dependence of water-solubility of the microplasma-treated SWCNTs

Based on the results obtained from FTIR, XPS and zeta potential measurements, we discuss the possible mecha-
nisms of pH dependence of water-solubility of the microplasma-treated SWCNTs. It has been revealed that the surface charge on SWCNTs and the resultant electrostatic repulsion force, which are enhanced under basic condition, seem to be most responsible for the pH dependence.

Regardless of the pH value, sidewalls of the SWCNT would be functionalized with -COO\(^-\) groups, which are introduced by the microplasma-generated O\(^\cdot\) radical and O\(_3\). After introduction of -COO\(^-\) groups on the SWCNT surface by the microplasma treatment, water-solubility of SWCNTs is influenced by the pH value as follows.

Under proton-rich acidic condition (initial pH \(\approx 3\)), -COO\(^-\) groups on SWCNT surface are protonated and change to -COOH groups. Since the protonation decreases negative electric charge on SWCNT surface, electrostatic repulsion force between SWCNTs may become smaller inducing their aggregation due to van der Waals force. Under neutral and basic conditions with higher pH values, the protonation of -COO\(^-\) groups is suppressed increasing the SWCNT surface charge and electrostatic repulsion force. Higher electrostatic repulsion can enhance SWCNT solubility in water preventing their aggregation. Similar mechanism of pH sensitive protonation and water solubility of SWCNT has been proposed in the preceding literatures [11-13]. Although the clear mechanism of these phenomena is under consideration, chemical reaction process between the SWCNT surface and active species (H\(^+\), O\(^\cdot\), and O\(_3\)), which were generated by the microplasma would play an important role.

4. Conclusions

The pH dependence of water-solubility of SWCNTs treated by the microplasma in aqueous solutions was improved by the microplasma treatment, however, the initial pH value of the suspension and highly dispersed SWCNT suspension was achieved under basic condition with higher initial pH value (pH > 10). Under acidic condition with lower initial pH value (pH < 4), however, the SWCNTs were aggregated. The microplasma-treated SWCNTs were more negatively charged under basic condition due to suppressed protonation of -COO\(^-\) groups. As a result, the electrostatic repulsion force between SWCNTs could overcome van der Waals force preventing their aggregation under basic condition.

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References