A simple method of fabricating carboxyl-terminated multiwalled carbon nanotubes (MWCNTs) with alkyl spacers was developed to improve the dispersion quality of MWCNTs in aqueous solutions using solution plasma (SP) in a 6-aminocaproic acid solution. The formation of SP in the solution led to better dispersion of MWCNTs in aqueous solutions. Fourier transform infrared spectroscopy (FT-IR) results indicate that a carboxyl group with an alkyl spacer can be introduced by SP treatment in the 6-aminocaproic acid solution. Sedimentation tests show that the SP-treated MWCNTs in the 6-aminocaproic acid solution retained their good dispersion quality in aqueous solutions of pHs 5, 6, and 9. The alkyl spacer plays an important role in the preservation of dispersion states particularly at pH 6. © 2017 The Japan Society of Applied Physics

1. Introduction

Carbon nanotubes (CNTs) are promising materials for various electronic devices and structural materials such as transparent and flexible thin displays[@1,2] and CNT-reinforced plastics[@3,4] as well as for energy applications such as electrodes in batteries and support for catalysts in fuel cells.[@5] Spin-casting processes and injection molding are the most promising fabrication methods for CNT thin films and complex three-dimensional (3D) shapes. However, the fabricated films tend to be non-uniform. The non-uniformity of films deteriorates their electronic properties and mechanical characteristics, and it originates from the wrong dispersion of CNTs in the suspensions used for the processing. Conventional pristine CNTs easily aggregate in aqueous solutions owing to their hydrophobicity, although CNTs can be dispersed in some organic solvents.[@6,7] From the viewpoint of industrial processing, improved suspensions have recently been expected in aqueous solution systems rather than organic solution ones owing to environmental requirements.

Essentially, the primary methods used to disperse CNTs in aqueous solutions consist of the control of the electric charge on the CNT surface, i.e., covering CNTs with adsorbed ionic dispersing agents[@8-10] and surface functionalization of CNTs with different chemical groups[@11-15]. The former method has quite simple processing steps. However, the ionic dispersing agents used frequently become impurities in the materials, and reduce and limit the properties of CNTs. The undesired properties and poor performances of CNT-based materials in application devices appeared. The latter method comparatively contains few impurities. However, the synthesis process is frequently complex and involves multiple steps. Also, the process requires the use of strong acids and bases or many organic solvents.

Solution plasma (SP) is nonequilibrium, low-temperature, atmospheric-pressure gas plasma generated by the liquid phase. Recently, SP has been widely utilized for nanomaterial synthesis and surface modification, e.g., metal nanoparticle synthesis[@16-18] nanocarbon synthesis[@19] heteroatom-nanocarbon synthesis[@20,21] and polymer degradation.[@22] Moreover, SP can quickly provide various functional groups, e.g., –COOH and –NH$_2$, to multiwalled CNTs (MWCNTs)[@23,24] through reactions as follows:

$$\text{MWCNTs}^{\text{SP}} \rightarrow \text{MWCNTs}^-\text{–COOH in distilled water,} \quad (1)$$

$$\text{MWCNTs}^{\text{SP}} \rightarrow \text{MWCNTs}^-\text{–NH}_2 \text{ in ammonia solution.} \quad (2)$$

In the reactions, the functional groups are directly introduced onto the CNT surface by SP treatments in simple solutions: distilled water or ammonia. These functional groups provide CNTs with electrostatic repulsive forces corresponding to a given pH. The SP-treated CNTs can be easily dispersed in aqueous solutions. However, the dispersion quality is not sufficiently good to improve the properties and performances of materials used in practical devices. The reason is simply due to the fact that CNTs have complex 3D winding and bending structures. Even when the repulsive force acts on CNTs, it acts point-to-point among the CNTs. Therefore, many contact points among CNTs exist owing to the winding and bending structures of CNTs. The contact points prevent the enhancement of separation among CNTs. Namely, not only the electrostatic repulsive force but also other factors are required for further promotion of dispersion.

Herein, we focused our attention on the effect of steric hindrance occurring when functional groups are introduced onto the CNT surface, i.e., the introduction of structural separators. Therefore, we aimed to obtain dispersibility-improved CNTs in aqueous solutions under mild pH conditions as possible. The strategy to realize additional improvement is to introduce a carboxyl-group-terminated alkyl spacer into CNTs through an SP process. Moreover, 6-aminohexanoic acid was utilized as a reaction agent to introduce a functional group into CNTs through the SP process. When this agent was used as a starting material in the SP process, it is expected to react with CNTs during the SP process through the following reactions:
the as-received MWCNTs were immersed in distilled water and reduced to small splinters through a shear treatment process. Next the carboxyl groups with an alkyl chain were attempted to be introduced into the MWCNTs by the SP treatment process in 6-aminohexanoic acid aqueous solution. The details of experimental procedures are described in following sections.

2.1 Materials
MWCNTs (Meijo Nano Carbon) and 6-aminohexanoic acid (97.0% purity, Wako Pure Chemical Industries) were used. Deionized pure water (H$_2$O) with a specific conductivity of 0.52 MΩ cm was prepared using a water demineralizer (Toyo Roshi RFD250NB). Approximately 1 g of MWCNTs was added into 200 mL of H$_2$O and suspended by stirring using an ultrasonication device. 6-Aminohexanoic acid was added into the solution containing MWCNTs. The concentration of 6-aminohexanoic acid was adjusted to 0.1 N.

2.2 Pretreatment
As-received MWCNTs were physically and tightly fouled. A shear process for the MWCNT samples was carried out as a pretreatment. Here, a wet pulverizing apparatus (Sugino Machine Star Burst Labo) was utilized to disintegrate the fouled MWCNTs. 2 L of 0.1 wt % MWCNT aqueous solution was injected and circulated into the apparatus. The treatment was carried out at 200 MPa pressure for 30 min.

2.3 Solution plasma treatment
A bipolar pulsed power supply (Kurita Seisakusho MPS-R06K01C-WP1-6CH) was used to generate and operate the solution plasma. A glass vessel was used as a reactor with two tungsten ($\phi$ = 1.0 mm, 99.95%, Nilaco) electrodes covered with insulating tubes, as shown in Fig. 2. SP was produced in the solutions containing MWCNTs with 6-aminohexanoic acid. The discharge conditions were as follows: the gap between the electrodes, 0.5 mm; repetition frequency, 20 kHz; pulse width, 2 μs; primary voltage, 100 V (breakdown voltage, ca. 1200 V); and discharge processing time, 1 h. During the discharge, MWCNTs were mixed well by stirring. After the treatments, all water-containing samples were dried using a
vacuum fumigation apparatus with a nitrocellulose membrane filter (pore diameter, 0.45 µm). The residual contaminations were removed by rinsing with water. The samples were finally dried again at 60 °C for 5 h in a vacuum drying furnace. MWCNTs in water without 6-aminohexanoic acid were treated with SP under the same conditions of the power supply to prepare a control sample.

2.4 Characteristics

The morphology of MWCNTs was observed by field-emission scanning electron microscopy (FE-SEM; Hitachi High-Technologies S-4800). The acceleration voltage was 10 kV, the current was 10 µA, and the working distance was 8.5 mm. The changes of the functional groups were evaluated by Fourier transform infrared spectroscopy (FT-IR; Thermo Fisher Scientific Nicolet 8700). Mercury cadmium telluride (MCT) was used as a detection diode with liquid N2. The observation space was purged with pure N2 gas from a N2 generator. The detection resolution was 1 cm$^{-1}$.

Sedimentation tests were performed for the sample solutions containing 1 wt% as-received MWCNTs, 1 wt% SP-treated MWCNTs in distilled water, and 1 wt% SP-treated MWCNTs in 6-aminohexanoic acid solution. The sample solutions were finally adjusted to pHs 5, 6, and 9 using HCl and NaOH solutions.

3. Results and discussion

3.1 Material characteristics

3.1.1 FE-SEM. FE-SEM images of (a) as-received MWCNTs and (b) pretreated MWCNTs with the wet pulverizing apparatus are shown in Fig. 3. FE-SEM observations were carried out to check for damage to the MWCNTs structure. From these images, no significant damage to the structure was observed. However, visual examination clearly shows that the pretreated MWCNTs have smaller grains than the as-received MWCNTs. Thus, this indicates that this treatment can unbind MWCNTs on the scale of more than 100 µm and retain the structures on the scale of less than 1 µm.

3.1.2 FT-IR. FT-IR measurements were conducted for SP-treated samples in distilled water and 6-aminohexanoic acid solution. The FT-IR spectra are shown in Fig. 4. The bands were assigned to (A) 3200–3550 [br; $\nu$(O–H, phenol)], (B) 3030 [v; $\nu$(C–H ip, aromatic)], (C) 2930 [s; $\nu$asy(CH2, alkyl)], (D) 2850 [s; $\nu$sy(CH2, alkyl)], (E) 1730 [s; $\nu$(C=O, associated amino)], (F) 1680–1700 [s; $\nu$(C=O, carboxylates)], (G) 1450–1600 cm$^{-1}$ [m; $\nu$(C=C, aromatic)], (H) 1370 [s; $\nu$as(CH3)]. In the spectrum of SP-treated MWCNTs in distilled water, all the bands except band (E) were observed. The SP-treated MWCNTs in distilled water have the functional groups of the phenol-type OH and the carboxyl-type OH. The presence of band (B) indicates that the in-plane C–H group terminates the edges of MWCNTs. However, partially, the edges of MWCNTs are also terminated by alkyl-based groups, as demonstrated by the presence of bands (C) and (D). These bands indicate the deterioration of the sp2 structure. The peaks frequently appeared in the FT-IR spectrum of MWCNTs.
owing to the disordered structures. Besides these bands, band (E) additionally appears in the spectrum of SP-treated MWCNTs in 6-aminohexanoic acid solution. This band indicates that amide bonds formed with MWCNTs. Moreover, bands (C) and (D) possibly became stronger in the case of SP-treated MWCNTs in 6-aminohexanoic acid solution. The presence of bands (C), (D), (E), and (F) guarantees the introduction of carboxyl functional groups with an alkyl spacer. On the other hand, band (A) became weaker in the case of SP-treated MWCNTs in 6-aminohexanoic acid solution. Apparently, it showed that the hydrophilicity property was lost. The decrease in the absorbance of band (A) is frequently observed in samples with the decrease in the number of hydrogen bonds among phenol-type OH and H$_2$O. From this viewpoint, the decrease in the absorbance of band (A) might originate from the decrease in the number of hydrogen bonds between MWCNTs since the distances between MWCNTs increase owing to the insertion of the alkyl spacer. However, changes in FT-IR spectra only do not provide evidence of the introduction of the carboxyl groups with an alkyl spacer. Herein, a possible product was confirmed from the dispersion and aggregation behavior during the segmentation test. The surface modification obtained from the FT-IR results provides an explanation of the dispersion and aggregation behavior of the SP-treated MWCNTs in distilled water and 6-aminohexanoic acid solution based on the changes in the electrostatic forces corresponding to given pHs and the volume exclusion effect.

### 3.2 Stability of suspension

The stability of MWCNT suspensions was revealed by the sedimentation tests of the solutions containing as-received MWCNTs and SP-treated MWCNTs in distilled water and 6-aminohexanoic acid solution. The sedimentation patterns of individual MWCNTs are shown in the photos in Fig. 5.

First, the sedimentation test in pH 6 solutions is discussed. In the suspensions of as-received MWCNTs and SP-treated MWCNTs in distilled water, the MWCNTs settled after only 5 min. On the other hand, SP-treated MWCNTs in 6-aminohexanoic acid solution remained dispersed in water after five days. This dispersion state arises from the repulsive force originating from the ionized functional group COO$^-$ on the MWCNT surface. Next, the sedimentation behavior at pHs 5 and 9 is discussed. In the suspensions of the as-received MWCNTs, the MWCNTs settled after only 5 min, whereas SP-treated MWCNTs in 6-aminohexanoic acid solution remained dispersed even after 5 days.

### Fig. 4. (Color online) FT-IR spectra of SP-treated MWCNTs in distilled water and 6-aminohexanoic acid solution.

### Fig. 5. (Color online) Sedimentation tests of the suspensions containing as-received MWCNTs, SP-treated MWCNTs in distilled water, and SP-treated MWCNTs in 6-aminohexanoic acid solution.
similarly to the suspension at pH 6. On the other hand, the SP-treated MWCNTs suspended in distilled water and 6-aminohexanoic acid solution had kept their initial dispersion state even after five days. Thus, the SP-treated MWCNTs in 6-aminohexanoic acid solution can keep their initial dispersion state in the pH range from 5 to 9. The SP-treated MWCNTs in distilled water cannot remain dispersed at pH 6. The as-received MWCNTs cannot maintain the dispersion in the entire range of pHs. Herein, at pH 6, a difference between the SP-treated MWCNTs in distilled water and 6-aminohexanoic acid solution provides us valuable information. To reveal the difference, the properties of conventional MWCNTs and functional groups are discussed. The zeta-potential of MWCNTs has a positive value under acidic condition (at low pHs) and the isoelectric point is located below pHs 6. The isoelectric point and the COOH functional group in the simple plane type of phenol is 9.95. The COOH− and −OH introduced onto the MWCNT surface are ionized at a given pH as follows:

\[
\begin{align*}
\text{MWCNTs} & \text{−COOH} \\
& \rightarrow \text{MWCNTs} \text{−COO}^- + \text{H}^+: \text{more than pHs 2−4}, \\
& \text{MWCNTs} \text{−OH (phenol type)} \\
& \rightarrow \text{MWCNTs} \text{−O}^- + \text{H}^+: \text{more than pHs 6−7}, \\
& \text{MWCNTs} \text{−OH (alcohol type)} \\
& \rightarrow \text{MWCNTs} \text{−O}^- + \text{H}^+: \text{more than pHs 7−8}.
\end{align*}
\]

Thus, the zeta-potential of the SP-treated MWCNTs became more negative with the increase in pH. Only from this point, the sedimentation at pH 6 of the SP-treated MWCNTs in distilled water cannot be explained, since the repulsive force increased with the increase in pH. Skwarek et al. investigated the effects of ions in the solution on the zeta-potentials of the CNTs and of the functional group introduced onto the CNT surface. They showed that the isoelectric point and aggregation size strongly depend on coexisting ions. When Na+ ions also exist in the solution, the isoelectric point shifted to a higher pH since small ions can exist inside the electronic double interlayer. For this, Na+ ions neutralize the zeta-potential, resulting in the aggregation of MWCNTs in the suspension. In particular, the effect might just be enhanced at approximately pH 6 in our system, although it depends on the ionic strength, the type of ions, co-existence of other kinds of ions, and so on. In contrast, the head groups were isolated by the alkyl spacers in the case of the SP-treated MWCNTs in 6-aminohexanoic acid solution. Therefore, when the body of MWCNTs is neutralized, the head groups maintain the repulsive force originating from the negative charge. This is the reason why the SP-treated MWCNTs in 6-aminohexanoic acid solution retained their initial dispersion state. The explanation is based on the electric shield effect induced by the spacer length. In this study, the spacer was introduced so that the volume exclusion effect of alkyl chains can enhance the repulsive effect. In fact, this maintains the electrostatic repulsive force against the environmental changes, as shown in Fig. 6.

4. Conclusions

In this study, we aimed to improve the dispersion quality of MWCNTs in aqueous solutions by the SP process. The SP treatment of the MWCNTs was performed in the solution containing distilled water and 6-aminohexanoic acid. The SP-treated MWCNTs in distilled water settled at pH 6, although they can be dispersed at pHs 5 and 9. On the other hand, the SP-treated MWCNTs in the solution containing distilled water and 6-aminohexanoic acid retained their excellent dispersion quality at pHs 5, 6, and 9. This difference was attributed to the presence of the alkyl spacer on the MWCNT surface and the carboxyl head group. The presence of the alkyl spacer led to the inhibition of the neutralization of the zeta-potential by the adsorption of cations on the MWCNT surfaces.

1) Z. Wu, Z. Chen, X. Du, J. M. Logan, J. Sippel, M. Nikolou, K. Kamaras, J. R. Reynolds, D. B. Tanner, A. F. Hebard, and A. G. Rinzler, Science 305, 1273 (2004).
2) G. Gruner, J. Mater. Chem. 16, 3533 (2006).
3) R. Andrews and M. C. Weisenberger, Curr. Opin. Solid State Mater. Sci. 8, 31 (2004).
4) J. N. Coleman, U. Khan, W. J. Blau, and Y. K. Gun’ko, Carbon 44, 1624 (2006).
5) M. F. L. De Volder, S. H. Tawfick, R. H. Baughman, and A. J. Hart, Science 339, 535 (2013).
6) K. D. Ausman, R. Piner, O. Louie, R. S. Ruoff, and M. Korobov, J. Phys. Chem. B 104, 8911 (2000).
7) B. J. Landi, H. J. Ruf, J. J. Worman, and R. P. Raffaelle, J. Phys. Chem. B 108, 17089 (2004).
8) J. Yu, N. Grossost, C. E. Koning, and J. Loos, Carbon 45, 618 (2007).
9) J. Rausch, R. C. Zhuang, and E. Mader, Composites, Part A 41, 1038 (2010).
10) M. D. Clark, S. Subramanian, and R. Krishnamoorti, J. Colloid Interface Sci. 354, 144 (2011).
11) H. Li, F. Cheng, A. M. Duft, and A. Adronov, J. Am. Chem. Soc. 127, 14518 (2005).
12) D. Tasis, N. Tagmatarchis, A. Bianco, and M. Prato, Chem. Rev. 106, 1105 (2006).
13) X. Peng and S. S. Wong, Adv. Mater. 21, 625 (2009).
14) P. Singh, S. Campidelli, S. Giordani, D. Bonifazi, A. Bianco, and M. Prato, Chem. Soc. Rev. 38, 2214 (2009).
15) I. Kumar, S. Rana, and J. W. Cho, Chem.—Eur. J. 17, 11092 (2011).
16) P. Pootawang, N. Saito, and O. Takai, Mater. Lett. 65, 1037 (2011).
17) M. A. Bratescu, S. P. Cho, O. Takai, and N. Saito, J. Phys. Chem. C 115, 24569 (2011).
18) A. Watthanaphanit, G. Panomsuwan, and N. Saito, RSC Adv. 4, 1622 (2014).
19) J. Kang, O. L. Li, and N. Saito, Carbon 60, 292 (2013).
20) G. Panomsuwan, N. Saito, and T. Ishizaki, Electrochem. Commun. 59, 81 (2015).
21) G. Panomsuwan, N. Saito, and T. Ishizaki, ACS Appl. Mater. Interfaces 8, 6962 (2016).
22) I. Prasertsung, S. Damrongzakkul, C. Terashima, N. Saito, and O. Takai, Carbohydr. Polym. 87, 2745 (2012).
23) K. Imasaka, Y. Kato, U. Khaled, and J. Suehiro, Jpn. J. Appl. Phys. 48, 065004 (2009).
24) T. Shirafuji, Y. Noguchi, T. Yamamoto, J. Hieda, N. Saito, O. Takai, A. Tsuchimoto, K. Nojima, and Y. Okabe, Jpn. J. Appl. Phys. 52, 125101 (2013).
25) G. Socrates, Infrared Characteristics Group Frequencies (Wiley, Chichester, U.K., 1994) 2nd ed., Chap. 2, 3, 5, 10, 11.
26) T. Ramanathan, F. T. Fisher, R. S. Ruoff, and L. C. Brinson, Chem. Mater. 17, 1290 (2005).
27) J. M. González-Domínguez, M. González, A. Ansón-Casasoa, A. M. Diez-Pascual, M. A. Gómez, and M. T. Martínez, J. Phys. Chem. C 115, 7238 (2011).
28) L. Zhao and L. Gao, Colloids Surf. A 224, 127 (2003).
29) C. Y. Kuo, Desalination 249, 781 (2009).
30) L. Chen and H. Xie, Thermochim. Acta 497, 67 (2010).
31) W. L. Marshall and E. U. Frank, J. Phys. Chem. Ref. Data 10, 295 (1981).
32) F. Rived, M. Roses, and E. Bosch, Anal. Chim. Acta 374, 309 (1998).
33) M. B. Smith and J. March, March’s Advanced Organic Chemistry: Reactions, Mechanisms, and Structure (Wiley, Hoboken, NJ, 2007) 6th ed., p. 385.
34) M. J. O’Neil, P. E. Heckelman, P. H. Dobbelaar, K. J. Roman, C. M. Kenny, and L. S. Karaffa, The Merck Index: An Encyclopedia of Chemicals, Drugs, and Biologicals (Royal Society of Chemistry, Cambridge, U.K., 2013) 15th ed., monograph numbers 427 and 7354.
35) F. Villacañas, M. F. R. Pereira, J. J. M. Órfão, and J. L. Figueiredo, J. Colloid Interface Sci. 293, 128 (2006).
36) E. Skwarek, Y. Boltbukh, V. Tertykh, and W. Janusz, Nanoscale Res. Lett. 11, 166 (2016).