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Functionalization of Multi-Walled Carbon Nanotubes Realized by Microwave-Driven Chemistry Inducing Dispersibility in Liquid Media

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Carboxyl groups have been successfully introduced to multi-walled carbon nanotubes by oxidation with a nitric acid or sodium hypochlorite aqueous solution under microwave irradiation. The introduced functional groups have been employed as a reactive terminus for introducing long alkyl chains to the surface of the nanotubes. The dispersibility in various solvents having different polarities can be controlled by the surface functionalization.

Carbon nanotubes (CNT) have attracted much attention, because an array of unprecedented structural, mechanical, and electronic properties has been demonstrated since their discovery.[1,2] CNT can exhibit a) metallic or semiconducting properties depending primarily on the roll-up vector, diameter, and helicity, b) chemical and thermal stability, c) extremely high tensile strength and elasticity, d) the ability to absorb gas molecules as nanocapillaries, and e) the potential of further chemical functionalization.[3] CNT can be classified into single-walled carbon nanotubes (SWCNT) and multi-walled carbon nanotubes (MWCNT).

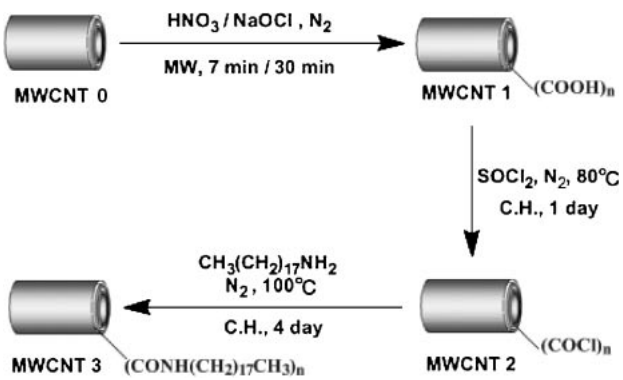
CNT cannot be dissolved or dispersed in solvent without chemical functionalization. Grafting solubility or dispersibility onto CNT is indispensable for applying CNT as a functional material, which also enables one to carry out both more extensive characterization and chemical syntheses.[4] However, in general, CNT has poor chemical reactivity due to the stable graphite-like structure, causing difficulty in chemical functionalization. There exist in the literature several reports on chemical functionalization of SWCNT using fluorine,[5] diazonium salts,[6] nitrene,[7,8] organic radicals,[9,10] and azomethine ylides.[11–14] These reactions require highly reactive reagents and long reaction times over 10 h.

On the other hand, only a few reports have appeared on MWCNT functionalization.[15] Much more severe reaction conditions are required for less-reactive MWCNT than SWCNT such as treatment under supercritical water[16] or supersonication in mixed acid.[17] Consequently, functionalized MWCNT has not been prepared through chemical treatment under conventional heating, due to its poor chemical reactivity.

In recent years, specific effects of microwave irradiation on chemical reactions have been demonstrated, i.e., enhancement of reaction rates, yields, and selectivities.[18–24] "Microwave-driven chemistry" has been applied to organic, inorganic, and materials chemistry.[25] Graphite is known to be heated rapidly to high temperatures by microwave irradiation. Recently, Mitra et al. and Yoshida and Sano have reported functionalization of SWCNT by oxidation under microwave irradiation.[26,27] But this can be carried out even by other conventional methods, since SWCNT is much more reactive than MWCNT.

In this paper, we report formation of carboxyl groups on the surface of MWCNT through oxidation with nitric acid or hypochloric acid not under conventional heating but under microwave irradiation. We should emphasize here again our aim, i.e., chemical functionalization of MWCNT with less chemical reactivity than SWCNT. Furthermore, the resulting carboxyl groups have been employed as a reaction terminal for chemically attaching long alkyl chains to the surface of CNT by reaction with alkylamines.

Chemical functionalization of MWCNT was performed according to Scheme 1. MWCNT was reacted with an oxidant (nitric acid or sodium hypochlorite) under microwave irradiation. The raw material was denoted as MWCNT **0**. Work up of the reaction mixture gave functionalized **1**, thus providing an expeditious access to a new family of functionalized MWCNT. Next, carboxyl groups of **1** were converted to an acyl chloride intermediate MWCNT$(COCl)_n$ (denoted as MWCNT **2**) by treatment with thionyl chloride and its subsequent reaction with an amine gave an amide MWCNT$(CONH(CH_2)_{17}CH_3)_n$ (denoted as MWCNT **3**).



Scheme 1. Synthesis of chemical functionalized MWCNT.

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Experimental

Measurements. Surface functionalization was elucidated by spectral, optical, and gravimetric methods. Fourier transform infrared spectroscopy was performed on a Perkin-Elmer 2000FT-IR spectrometer. Raman spectroscopy was performed on a JEOL JRS-FT7000N instrument using a He-Ne laser with a wavelength of 632.8 nm. UV–vis spectra were obtained using a Hitachi High-Technologies U-3300 spectrophotometer. The extent of surface carboxylation by oxidation under microwave irradiation was estimated by thermogravimetric analysis (TGA) using a Shimadzu TGA-50 analyzer. TGA was performed under nitrogen at a heating rate of 10 °C min^{-1}. Scanning electron microscopy (SEM) was used to investigate the bundles of MWCNT using a JEOL JSM-6700F instrument. The sizes and morphologies were characterized by a transmission electron microscopy (TEM) at 200 kV using a Hitachi H-800 instrument (Hitachi High-Technologies Co.). A diluted methanol solution of MWCNT was dropped onto a copper grid coated with carbon film, and then dried under vacuum at 398 K.

Preparation of Functionalized MWCNT. MWCNT was purchased from Sigma-Aldrich (90% purity). SEM observation showed the average diameter and length of the material in our sample to be about 20 to 50 nm and several μm, respectively. A focused single-mode microwave synthesis system (Discover, CEM, USA, 2.45 GHz) was used for irradiating reaction mixtures. MWCNT **1** was obtained by the two methods described below. In the first procedure, MWCNT (100 mg) was oxidized in a solution of sodium hypochlorite (3 mL, 12%) under microwave irradiation at 200 W for 30 min at ambient pressure. After centrifugation, the supernatant was decanted and the remaining solid was washed with sulfuric acid and methanol three times. The resulting solid was dried at room temperature under vacuum. In the second method, MWCNT was treated with nitric acid as an oxidant under elevated pressure. Oxidation of the substrate (100 mg) in concentrated nitric acid (3 mL, 70%) under microwave irradiation at 200 W for 7 min was conducted under 1.0×10^6 Pa pressure. As a reference, MWCNT (100 mg) was treated in concentrated nitric acid (3 mL, 70%) by conventional heating (denoted as MWCNT (conv.)).

MWCNT **3** was prepared as follows: 100 mg of MWCNT **1** was stirred in 20 mL of thionyl chloride with dimethylformamide (1 mL) at 70 °C for 24 h. The resulting mixture was then distilled to remove thionyl chloride. After washing the resulting dispersion with anhydrous THF, the supernatant was decanted and the remaining solid was washed with ether three times. The remaining solid (MWCNT **2**) was dried at room temperature under vacuum. The resulting MWCNT **2** was heated with 2 g of octadecylamine (ODA, mp 55 to 57 °C) at 100 °C for 48 h. After cooling to room temperature, the excess ODA was removed by washing with ethanol four times under sonication (42 KHz). The remaining solid (MWCNT **3**) was dried at room temperature under vacuum.

Results and Discussion

Introduction of Carboxyl Group to MWCNT. Progress of the carboxylation was observed by FT-IR spectroscopy. KBr pellets were prepared from sample aliquots taken at periodic intervals with the results being displayed in Figs. 1 and 2. Although considerable noise was observed in the spectra due to the high magnification of the weak spectra, a peak at ca. 1580 cm^{-1} was observed corresponding to C=C stretching vi-

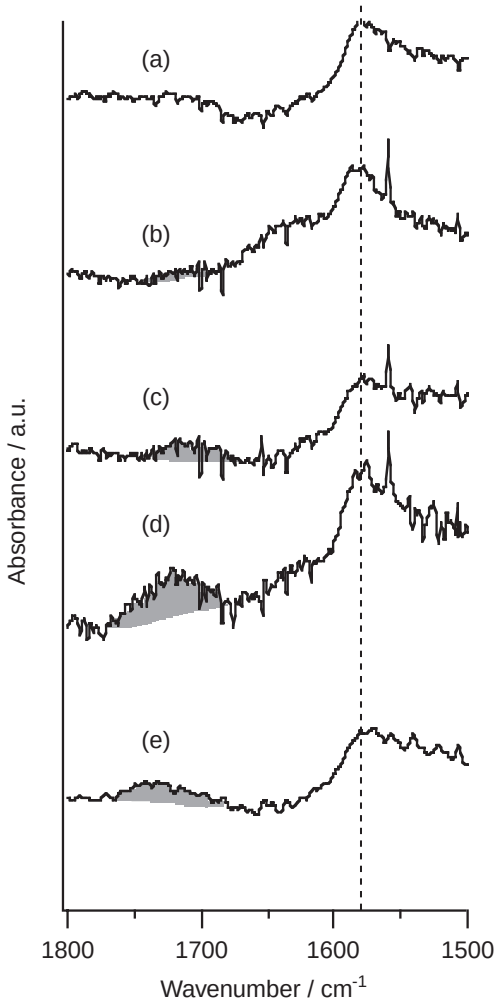

Fig. 1. IR spectra of MWCNT **0** (a) and MWCNT **1**/HNO_3. MW irradiation time: 1 min (b), 3 min (c), 7 min (d), and 20 min (e).

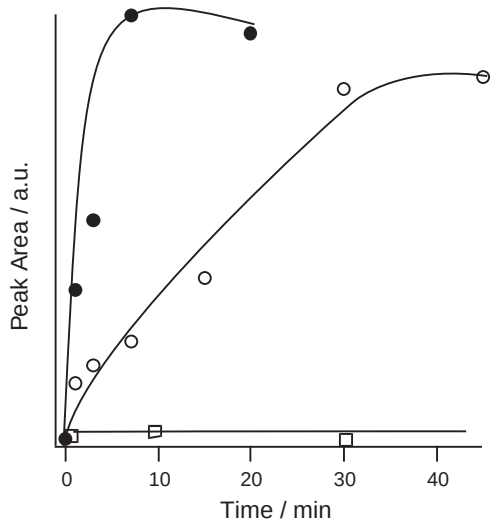

Fig. 2. Increase in the IR peaks attributed to carboxyl groups formed on MWCNT **1**/HNO_3 (closed circles), MWCNT **1**/NaOCl (open circles), and MWCNT (conv.) (open square).

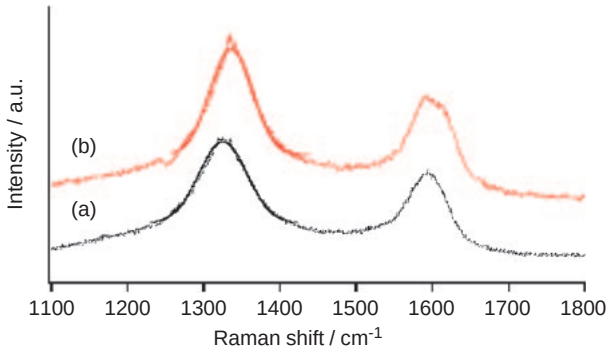

Fig. 3. Raman spectrum of MWCNT **0** (a) and MWCNT **1** (b).

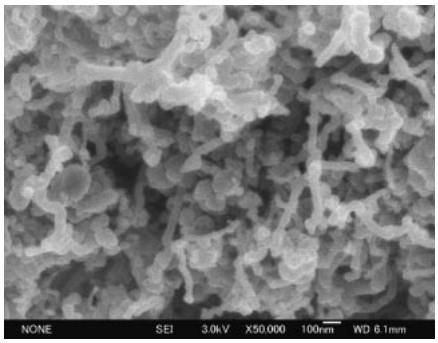

Fig. 4. SEM image of MWCNT **1**.

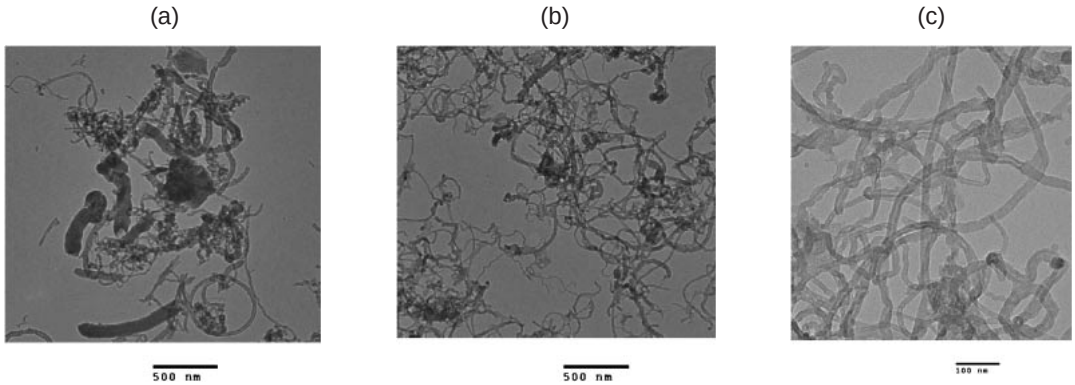

Fig. 5. TEM images of MWCNT **0** (a) and MWCNT **1** (b), and close view of MWCNT **1** (c).

brations. A weak absorbance around 1720 cm^{-1} was assigned to the C=O stretching vibration of the carbonyl groups,[4] indicating the extent of carboxylation. Figure 1 illustrates the change in the IR spectrum over time in the nitric acid mediated reaction. The intensity increased with the progress of irradiation time and decreased after reaching a maximum with further irradiation.

Figure 2 shows the changes of the integrated peak areas of carboxyl groups formed on MWCNT treated with nitric acid or sodium hypochlorite aq. The formation of carboxyl groups was more rapid for the sample treated with nitric acid than with sodium hypochlorite. The amount of carboxyl groups formed by treatment with nitric acid reached a maximum at 7 min and then gradually decreased after further treatment, probably due to partial decomposition under extremely severe oxidative conditions. When a sodium hypochlorite solution was used as an oxidant, the amount of carboxyl groups gradually increased and reached saturation at 30 min, probably due to limited reaction sites. It is assumed that the oxidation reaction takes place only at open ends and defects of MWCNT,[16] explaining the similar saturated amounts of carboxyl groups formed by treatments with nitric acid and sodium hypochlorite aq. We have demonstrated that the formation of carboxyl groups through oxidation of MWCNT was complete in an extremely short time. On the other hand, no increase in the IR peaks attributed to carboxyl groups formed on MWCNT (conv.) was observed, indicating that the functionalizing reaction for MWCNT did not proceed under conventional heating at all (Fig. 2).

The Raman spectra of MWCNT **0** and MWCNT **1** were examined to confirm functionalization of the substrate (Fig. 3). Two characteristic features have been observed in the Raman spectra of MWCNT **0** and MWCNT **1**. The peaks around 1583 cm^{-1} of MWCNT **0** and MWCNT **1** were assigned to the G-band originating from the tangential oscillation of the carbon atoms in MWCNT. Another peak around 1326 cm^{-1} of MWCNT **0** was assigned to the D-band, associated with a decrease in symmetry reflecting the presence of defects in MWCNT. The D-band peak of MWCNT **1** was shifted to 1336 cm^{-1} by 10 cm^{-1}. In order to estimate the decrease of symmetry induced by the chemical functionalization, we compared the ratios of the integrated areas of D-band and G-band, i.e., I_D/I_G, between MWCNT **0** and MWCNT **1**. The calculated I_D/I_G ratios of MWCNT **0** and MWCNT **1** were 1.30 and 1.45, respectively. The high I_D/I_G ratio of MWCNT **1** compared with that of MWCNT **0** showed the decrease in symmetry in the structure of MWCNT **1** as a result of the introduction of carboxyl groups to the surface of MWCNT **1**.

The SEM image of MWCNT **1** showed that the morphology of MWCNT did not change after oxidation, indicating no severe degradation occurring to MWCNT **1** (Fig. 4). The TEM images of MWCNT **0** and MWCNT **1** are shown in Fig. 5. As shown in Fig. 5a, MWCNT **0** aggregated in bundles with diameters of 20–200 nm. On the other hand, it has been confirmed that no large diameter bundles were observed for MWCNT **1** (Fig. 5b). As shown in Fig. 5c, the functionalized MWCNT **1** was converted into thin bundles or individual threads with a diameter of 10–30 nm. This result indicated that carboxyl groups on the surface of MWCNT **1** effectively prevented carbon nanotubes from bundling and/or aggregating.

In order to estimate the weight content of carboxyl groups on the surface of MWCNT, TGA measurements of MWCNT **0** and the functionalized MWCNT **1** were carried out. Figure 6

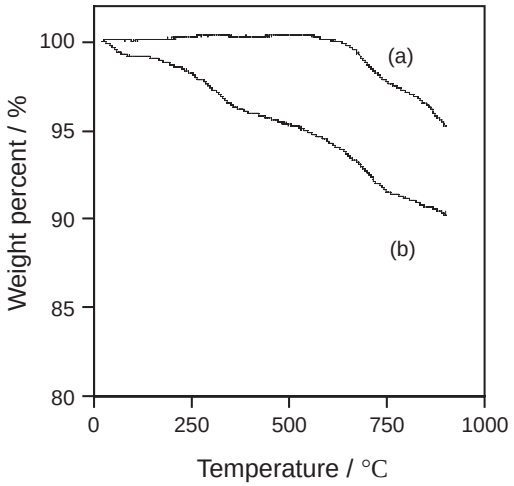

Fig. 6. TGA measurement of MWCNT **0** (a) and MWCNT **1** (b) with a heating rate of 10 °C min^{-1} at the nitrogen flow rate of 50 mL min^{-1}.

shows the weight loss curves of MWCNT **0** and MWCNT **1**. The weight loss of MWCNT **0** derived from the combustion of carbon nanotubes was observed above 550 °C. The weight loss observed in the 150–550 °C for MWCNT **1** could be attributed to decomposition of carboxyl groups on the surface of MWCNT **1** accompanied by release of carbon dioxide. The weight content of carboxyl groups of MWCNT **1** calculated on the basis of weight loss observed in the TGA data was about 5 wt %.

Difference of Reactivity for Functionalization between MWCNT and SWCNT. Mitra et al. have reported the chemical functionalization of single-walled CNT (SWCNT). They prepared the functionalized SWCNT (SWCNT **1**) by oxidation of 20 mg of SWCNT obtained from Carbon Nanotechnologies in 20 mL of a 1:1 mixture of 70% nitric acid and 97% sulfuric acid for 3 min under microwave irradiation at 450 W with 0.14×10^6 Pa of pressure.[26] We applied the same synthesis approach to MWCNT. MWCNT/HNO_3, H_2SO_4 was prepared by oxidation of MWCNT (20 mg) in a 1:1 mixture of concentrated nitric acid (10 mL, 70%) and sulfuric acid (10 mL, 97%) under microwave irradiation at 450 W for 10 min with 0.14×10^6 Pa of pressure (denoted as MWCNT **4**). The FT-IR spectrum of MWCNT **4** is shown in Fig. 7. No peak at 1720 cm^{-1} assignable to the C=O stretching vibration of carboxyl groups could be observed for that of MWCNT **4**, clearly indicating that functionalization of MWCNT could not be achieved by the same synthetic approach as the functionalization of SWCNT under microwave irradiation. Consequently, we have succeeded in preparing the functionalized MWCNT **1** under microwave irradiation under seven-fold higher pressure (1.0×10^6 Pa) in comparison with that of the functionalized

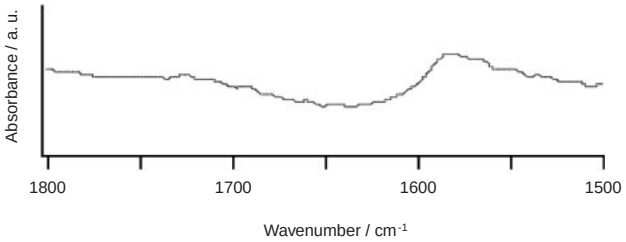

Fig. 7. FT-IR spectra of MWCNT **4** under microwave irradiation with 0.14×10^6 Pa.

SWCNT (Table 1).

The degree of carbonylation of functionalized SWCNT and MWCNT were compared using the results of the TGA measurements. Though the synthesis conditions for functionalizing MWCNT **1** were much more severe than for functionalizing SWCNT **1**, the amount of carboxyl groups formed on SWCNT **1** (nearly 50 wt %)[26] was much larger than that of MWCNT **1** (nearly 5 wt %). This indicates that the active reaction sites for MWCNT are rather scant compared to those of SWCNT. Here, we explain the lower reactivity of MWCNT than SWCNT in the following manner: MWCNT easily forms aggregates due to strong intermolecular van der Waals interactions among the nanotube threads, suppressing exposure of the active reaction sites present on the side walls and tube ends.

Introduction of Amide Group to MWCNT. The carboxyl groups prepared on the surface were used as a reactive terminal for further chemical functionalization. Figure 8 shows changes in the FT-IR spectra for MWCNT **0**, MWCNT **1**, and MWCNT **3**, acquired in KBr pellets. The spectrum of MWCNT **0** indicated only C=C stretching at ca. 1580 cm^{-1} (Peak A, shown in Fig. 8a). The spectrum of MWCNT **1** showed a peak at 1720 cm^{-1} attributed to the C=O stretching vibration of newly formed carboxyl groups (Peak B, shown in Fig. 8b). The shift of the C=O stretching vibration to a wavenumber lower by 20 cm^{-1} observed for MWCNT **2** (not shown in the figure) should be due to replacement of –OH with Cl, supporting the conversion of carboxyl groups to acyl chloride. The spectrum of MWCNT **3** displayed new absorption peaks attributed to the C=O stretching vibration of amide groups at 1620 cm^{-1} (Peak C, shown in Fig. 8c) and C–H vibration around 3000–2800 cm^{-1} derived from long alkyl chains, proving the formation of MWCNT **3**. However, peak B attributed to C=O stretching vibration of carboxyl groups still remained in Fig. 8c. Therefore, this amidation reaction of MWCNT **2** with ODA has proceeded by partial conversion of carboxyl groups to amide groups.

Figure 9 shows the UV–vis spectra of MWCNT **0**, MWCNT **1**, and MWCNT **3**, dispersed in methanol. The broad band around 277 nm was assigned to the π–π^* transition of

Table 1. Reaction Conditions and Weight Ratio of the Carboxyl Group of the Functionalized SWCNT and the Functionalized MWCNT

	Oxidant	Reaction time /min	MW power /W	Pressure /10^6 Pa	–COOH /wt %	Functionalization
SWCNT	HNO_3, H_2SO_4	3	450	0.14	50	◎
MWCNT **1**	HNO_3	7	200	1	5	○
MWCNT **4**	HNO_3, H_2SO_4	10	450	0.14	0	×

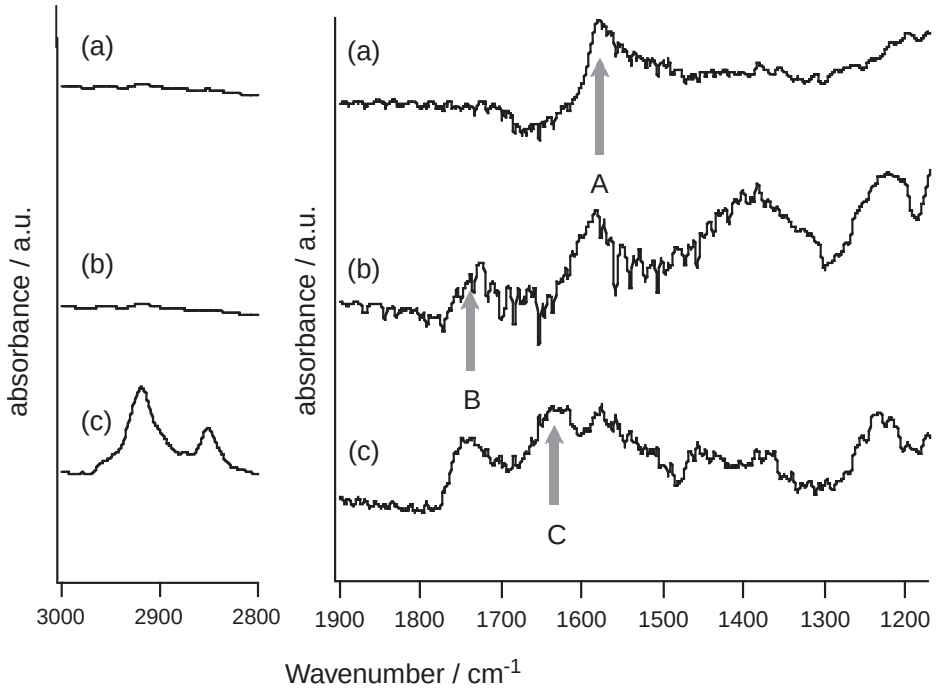

Fig. 8. FT-IR spectra of MWCNT **0** (a), MWCNT **1** (b), and MWCNT **3** (c).

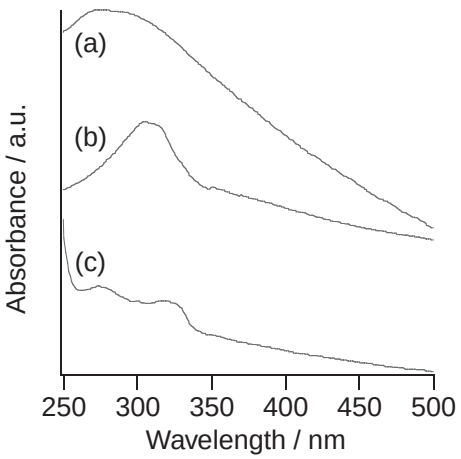

Fig. 9. UV–vis spectra of MWCNT **0** (a), MWCNT **1** (b), and MWCNT **3** (c) in methanol.

MWCNT **0**. After the introduction of carboxyl groups, the peak apex of the π–π^* transition was shifted from 277 to 303 nm in MWCNT **1**. Furthermore, after the amidation described above, two characteristic peaks of MWCNT **3** appeared at 276 and 325 nm, while the weak peak observed at 303 nm for MWCNT **1** still remained. These changes observed in the UV–vis spectra suggest that the functionalization of the surface should affect the electronic configurations of the π systems in MWCNT.

Dispersibility of Functionalized MWCNT. In order to examine the dispersibility of the functionalized MWCNT in solvents induced by introducing carboxyl groups and long chain alkyl groups, changes in the absorbance of the UV–vis spectra of MWCNT **0**, MWCNT **1**, and MWCMT **3** (1 mg) dispersed in water, acetone, and hexane (20 mL) were recorded at 600 nm with standing time as shown in Fig. 10.

MWCNT **0** could not be dispersed stably in water as shown in Fig. 10A: the absorbance of MWCNT **0** was decreased by 95% within 1.5 h. On the other hand, the absorbance of MWCNT **1** was largely maintained at the starting absorbance after 1.5 h. Even after 24 h, the absorbance of MWCNT **1** showed only a decrease of 10%. Functionalization of the surface with octyl groups through amidation (MWCNT **3**) gave the dispersion stability in water, which was better than pristine MWCNT **0**, but worse than MWCNT **1**: the absorbance of MWCNT **3** was decreased by 35% after 1.5 h. The striking changes in the dispersibility could be ascribed to drastic changes in the hydrophilicity of the surface of MWCNT by adding carboxyl groups and long chain alkyl groups. Consequently, when water was used as a solvent, the dispersibility order followed MWCNT **1** > MWCNT **3** $\gg$ MWCNT **0**.

When a similar experiment was carried out with acetone as a solvent, the dispersibility followed the order of MWCNT **3** > MWCNT **1** $\gg$ MWCNT **0**. Alkyl groups with hydrophobic character in MWCNT **3** should enhance the dispersibility in a relatively hydrophobic solvent, acetone. The surface functionalization with carboxyl groups through oxidation and alkyl groups through amidation did not show remarkable enhancement in the dispersibility in hexane, though the addition of alkyl groups induced a notable increase in the dispersion although to a low extent. It was considered that the dispersion of MWCNT in completely hydrophobic solvents such as hexane would suffer from the presence of polar carbonyl groups as a moiety of the functional groups.

Summary

In summary, we have succeeded in the surface functionalization of unreactive MWCNT through oxidation under microwave irradiation under 1.0×10^6 Pa of pressure, attaching carboxyl groups and long alkyl chains to the surface. The surface

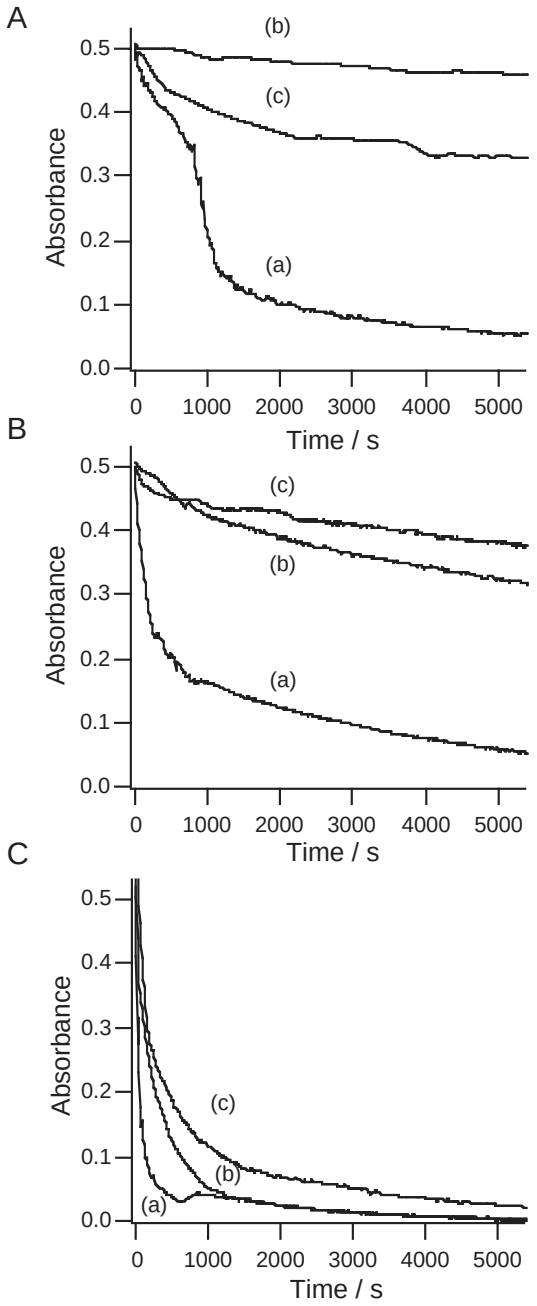

Fig. 10. Changes of the absorbance at 600 nm observed for the dispersions of MWCNT **0** (a), MWCNT **1** (b), and MWCNT **3** (c) with standing in water (A), acetone (B), and hexane (C).

functionalization can enhance the solvent dispersibility depending on the compatibility of the pendant functional groups and the solvent. We have demonstrated microwave-driven chemistry as a new technique for inducing chemical reactions in recalcitrant multi-walled nanotubes. This new approach could open a new door to the chemistry of new functional materials of CNT.

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