Magnetic orientation of single-walled carbon nanotubes or their composites using polymer wrapping

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Abstract
The magnetic orientation of single-walled carbon nanotubes (SWNTs) or the SWNT composites wrapped with polymer using poly[2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylene vinylene] (MEHPPV) as the conducting polymer were examined. The formation of SWNT/MEHPPV composites was confirmed by examining absorption and fluorescence spectra. The N,N-dimethylformamide solution of SWNT/MEHPPV composites or the aqueous solution of the shortened SWNTs was introduced dropwise onto a mica or glass plate. The magnetic processing of the composites or the SWNTs was carried out using a superconducting magnet with a horizontal direction (8 T). The AFM images indicated that the SWNT/MEHPPV composites or the SWNTs were oriented randomly without magnetic processing, while with magnetic processing (8 T), they were oriented with the tube axis of the composites or the SWNTs parallel to the magnetic field. In polarized absorption spectra of SWNT/MEHPPV composites on glass plates without magnetic processing, the absorbance due to semiconducting SWNT in the near-IR region in horizontal polarized light was almost the same as that in vertical polarized light. In contrast, with magnetic processing (8 T), the absorbance due to semiconducting SWNT in the horizontal polarization direction against the direction of magnetic field was stronger than that in the vertical polarization direction. Similar results were obtained from the polarized absorption spectra for the shortened SWNTs. These results of polarized absorption spectra also support the magnetic orientation of the SWNT/MEHPPV composites or the SWNTs. On the basis of a comparison of the composites and the SWNTs alone, the magnetic orientation of SWNT/MEHPPV composites is most likely ascribable to the anisotropy in susceptibilities of SWNTs.

Keywords: magnetic orientation, magnetic processing of single-walled carbon nanotube, polymer wrapping, composite material, conducting polymer, AFM, polarized absorption spectrum, magnetic susceptibility

(Some figures in this article are in colour only in the electronic version)
1. Introduction

Since the discovery of single-walled carbon nanotubes (SWNTs), they have been expected to become building blocks of next generation functional nanomaterials. However, their strong cohesive property and poor solubility have been restricting their application to fundamental and applied research fields. One of the methods of overcoming these problems is to make the SWNTs soluble in solvents by wrapping them with polymers [1]. At the same time, the fabrication of high-performance carbon-nanotube (CNT)-based composites is driven by the ability to create anisotropy at the molecular level to obtain appropriate functions.

Many groups have reported the orientation of CNTs by several methods, such as spinning of CNTs [2], condensing of viscous flow-aligned polymer-CNT composites [3], applying electric field [4, 5], and using the cooperative reorientation of a liquid-crystal-CNT suspension in electric field [6]. Several groups have reported magnetic orientation of CNTs using strong magnetic fields [7–10]. However, the magnetic orientation of composites between CNT and a conducting polymer have rarely been reported.

In addition, SWNTs have been expected to act as acceptors or molecular wires in molecular photoelectric conversion since SWNTs have attractive electron-accepting properties and a one-dimensional nanowire structure. Recently, the photoelectrochemical reactions between composite-modified electrodes and photosensitizers, such as semiconductor or donor molecules, have been reported in some papers [11–13]. For example, novel SWNT composites obtained via electrostatic interaction using poly(sodium 4-styrenesulfonate) (PSS) or pyrene derivatives have been reported in several papers [11, 12, 14–16]. Recently, we examined photoelectrochemical reactions of a modified electrode with composite materials consisting of poly[2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylene vinylene] (MEHPPV) as a conjugated polymer or ruthenium tris(2,2′-bipyridine) (Ru(bpy)₃²⁺)-PSS complex and SWNT [17]. The magnetic orientation of these composites on the electrodes is expected to improve the photoelectrochemical properties of the electrodes.

In this study, we have examined the magnetic orientation of the SWNTs or the polymer-wrapped SWNTs using MEHPPV by measurements of AFM images and polarized absorption and fluorescence spectra.

2. Experimental procedure

SWNTs (HiPco, Carbon Nanotechnologies Incorporated) were shortened by ultrasonication using a probe-type sonicator (Branson model 250) and a mixture of acids (H₂SO₄ and HNO₃) with ice-cooling. After diluting the mixture with water (MiliQ), the shortened SWNTs were purified by filtration though a PTEE membrane filter (pore size: 1 or 0.2 µm) or by chromatography (Sepadex G-50).

The SWNT/MEHPPV composites were prepared by the following procedure. The shortened SWNTs (about 0.1 mg) were added to the DMF solution (1.4 µM) of MEHPPV (Aldrich, average Mn = 40 000 ~ 70 000). Then, the suspension was sonicated with a bath-type sonicator (Branson model 1510). Centrifugation (6000 rpm) of the suspension for 15 min gave the DMF solution of the SWNT/MEHPPV composite.

The shortened SWNTs (about 0.1 mg) were added to the aqueous solution in the absence and the presence of NaHCO₃ (0.1 M). Then, the suspensions of the shortened SWNTs in the absence and the presence of NaHCO₃ were sonicated with a bath-type sonicator (Branson model 1510). Centrifugation (6000 rpm) of the suspensions for 15 min gave the aqueous solution of the shortened SWNTs in the absence and the presence of NaHCO₃.

A superconducting magnet (Oxford Instrument, Spectromag-1000) was used in the experiments of horizontal magnetic field, as reported in the previous papers [7, 8]. In the superconducting magnet a bore tube (50 mm φ) was installed horizontally. The distribution of the magnetic field was approximated with a Gaussian distribution. The maximum strength of the magnetic field was 8.0 T at the center position [7, 8]. The direction of magnetic field was horizontal.

Measurements of magnetic processing were carried out by the following procedure. The DMF solution of the SWNT/MEHPPV composite was introduced dropwise onto freshly cleaved mica or a glass plate. The aqueous solutions of the shortened SWNTs in the absence and the presence of NaHCO₃ were also introduced dropwise onto the mica or the glass plate. The magnetic field was applied during the evaporation of solvents, using the above superconducting magnet. Samples placed in the absence of magnetic field (outside of the bore tube) were used as controls.

After drying at 283 K, the AFM images of the SWNT/MEHPPV composites and the shortened SWNTs on mica were recorded in contact mode using a Nanoscope IIIa (Digital Instrument). The polarized absorption spectra of the SWNT/MEHPPV composites and the shortened SWNTs on glass plates were measured using a UV-VIS-NIR scanning spectrometer with a polarizer and sample-immobilization set, as described below.

![Scheme 1. Chemical structure of MEHPPV.](image)
3. Results and discussion

3.1. Absorption and fluorescence spectra of SWNT/MEHPPV composites

Absorption spectra of MEHPPV and MEHPPV added to SWNTs (about 0.1 mg) in DMF were measured to examine the formation of SWNT/MEHPPV composites (figure 1(A)). In the addition of SWNT, after the procedure described in the experimental procedure section, the absorption spectrum (figure 1(A)(a)) of the SWNT-MEHPPV system is different from that (figure 1(A)(b)) of MEHPPV because of the dissolution of SWNTs. The characteristic absorption bands in the near-IR region (figure 1(B)), owing to the interband transition between the mirror image spikes in the density of states of SWNTs [19], in other words, as a result of the semiconducting SWNT, were observed. Therefore, figure 1 clearly shows that MEHPPV rendered the SWNTs soluble in DMF, and the formation of SWNT/MEHPPV composite occurred.

The shortened SWNTs were soluble in aqueous solutions in both the absence and the presence of NaHCO
3 in the experimental section. The absorption spectrum of SWNT in the presence of NaHCO
3 was similar to that in the absence of NaHCO
3. However, in the presence of NaHCO
3, the shortened SWNTs were highly soluble in aqueous solution compared with those in the absence of NaHCO
3, owing to acid dissociation of the terminal carboxyl group of the shortened SWNTs as a result of the addition of NaHCO
3.

Fluorescence spectra of MEHPPV and MEHPPV added to SWNT in DMF were also measured to examine the formation of SWNT/MEHPPV composite (figure 2). The fluorescence band due to MEHPPV was observed at 550 nm in DMF solution of MEHPPV. In the addition of SWNT, the fluorescence intensity decreased drastically compared with that of only MEHPPV. Three peaks (583, 605 and 654 nm) in the fluorescence spectrum of MEHPPV were observed, which are different from those of MEHPPV. These results indicate that there are strong interactions between MEHPPV and SWNT and photoinduced electron transfer from the singlet excited state of MEHPPV to SWNT occurs. The results of fluorescence spectra also support the formation of SWNT/MEHPPV composite, as suggested by the absorption spectra [17].

3.2. AFM images with and without magnetic processing

AFM images of the SWNT/MEHPPV composites on the mica, after drying at 283 K under a magnetic field of 8 or 0 T (control), were measured (figure 3). The heights of the top of SWNT/MEHPPV composites were 6–15 nm (figure 3(c)). The results indicate that SWNT/MEHPPV composites consist of bundles of 4–21 SWNTs, since the diameter of the SWNTs is 0.7–1.5 nm.

The AFM images strongly indicate that the SWNT/MEHPPV composites are oriented randomly without magnetic processing (0 T) (figure 3(a)), but oriented with the tube axis of the composites parallel to the magnetic field with magnetic processing (8 T) (figure 3(b)). We examined the effect of the length of the shortened SWNT on the magnetic orientation of the SWNT/MEHPPV composites. In the long SWNTs (average length 2.2 µm), the magnitude of
Figure 3. AFM images of SWNT/MEHPPV composites on mica placed in (a) 0 and (b) 8 T. (c) cross-sectional profiles along line in AFM image at 8 T.

Figure 4. AFM images of shortened SWNTs in the absence of NaHCO$_3$ on mica placed in (a) 0 and (b) 8 T. AFM images of the shortened SWNTs in the presence of NaHCO$_3$ (0.1 M) on mica placed in (a) 0 and (b) 8 T.

The magnetic orientation (figure 3(b)) was larger compared with that in the short SWNTs (average length: 1.3 $\mu$m) in the AFM measurement.

The AFM images of the shortened SWNTs in the absence of NaHCO$_3$ on mica were also measured after drying at 283 K under a magnetic field of 8 or 0 T (control) (figure 4). The AFM images of the shortened SWNTs in the absence of NaHCO$_3$ strongly indicate that the SWNTs are oriented randomly without magnetic processing (0 T) (figure 4(a)), while the SWNTs are oriented with the tube axis of the composites parallel to the magnetic field with magnetic processing (8 T) (figure 4(b)). In addition, the AFM images of the shortened SWNTs in the presence of NaHCO$_3$ strongly indicate that the SWNTs are oriented randomly without magnetic processing (0 T) (figure 4(c)), while the SWNTs are oriented with the tube axis of the SWNT parallel to the magnetic field with magnetic processing (8 T) (figure 4(d)). Therefore, the magnetic orientation of the SWNTs is achieved by applying a strong magnetic field (8 T) with a horizontal direction.

On the basis of the results of comparing AFM images of the SWNT/MEHPPV composites and the SWNT in the absence and the presence of NaHCO$_3$ (figures 3 and 4), the magnetic orientation of SWNT/MEHPPV composites is most likely ascribable to the anisotropy in the susceptibility of SWNTs.

3.3. Polarized absorption and fluorescence spectra without and with magnetic processing

Polarized absorption spectra of the SWNT/MEHPPV composites on glass plates were measured in the near-IR region (900–1600 nm) using an UV-VIS-NIR spectrometer. Without magnetic processing (0 T), the absorbance of the band (at about 1150 nm) due to the semiconducting SWNT was almost the same in both polarization directions (horizontal and vertical) (figure 5(a)). On the other hand, with magnetic processing (8 T), the absorption band of the SWNT/MEHPPV composites and the SWNT in the semiconducting state was almost the same in both polarization directions (horizontal and vertical) (figure 5(a)). The absorption bands of the SWNT/MEHPPV composites on the glass plate are similar to those in the case of DMF solution (figure 1(B)). On the other hand, with magnetic processing (8 T), the absorption band (at about 1150 nm) of the SWNT/MEHPPV composites on the glass plates in the horizontal polarization direction...
against the direction of magnetic field (H||; 0°) was larger than that in the vertical polarization direction (H⊥; 90°) (figure 5(b)).

Next, polarized absorption spectra of the shortened SWNTs in the presence of NaHCO₃ on the glass plates were measured in the near-IR region (1000–1600 nm). In the absence of magnetic processing, the absorption band (at about 1450 nm) due to the semiconducting SWNT was observed in both polarization directions (horizontal and vertical) (figure 6(a)). The absorption bands on the glass plate are similar to those in the case of aqueous solution. In contrast, in the presence of magnetic processing (8 T), the absorbance (at about 1450 nm) due to the semiconducting SWNT in the horizontal polarization direction against the direction of magnetic field (H||; 0°) is much greater than that in the vertical polarization direction (H⊥; 90°) (figure 6(b)).

In the case of the shortened SWNTs in the absence of NaHCO₃, the absorption band (at about 1000 nm) due to the semiconducting SWNT was also observed in both polarization directions (horizontal and vertical) without magnetic processing, similar to those in figure 6(a).

On the other hand, with magnetic processing (8 T), the absorbance due to the semiconducting SWNT in the horizontal polarization direction against the direction of magnetic field (H||; 0°) was much greater than that in the vertical polarization direction (H⊥; 90°) (figure 6(c)). The peaks of absorption (at about 1000 nm) in figure 6(c) are different from those (at about 1450 nm) in figures 6(a) and (b). The result is ascribable to the difference in the electronic properties of the shortened SWNTs owing to the cutting in the acid mixture.

The above results of polarized absorption spectra on glass plates confirm the magnetic orientation of the SWNT/MEHPPV composites and the shortened SWNTs in the absence and the presence of NaHCO₃, where the composites or the SWNTs were oriented with the tube axis parallel to the magnetic field (8 T), was achieved, indicated by the results of the AFM images (figures 3 and 4).

On the basis of the polarized absorption spectra (figures 5 and 6), the magnetic orientation of SWNT/MEHPPV composites is also most likely ascribed to the anisotropy in the susceptibility of SWNTs, similar to the results obtained from AFM images (figures 3 and 4) as described above.

We preliminarily examined polarized fluorescence spectra for the MEHPPV in the SWNT/MEHPPV composites on glass plates without and with magnetic processing (8 T). The polarization degree (P-value) of the fluorescence for the MEHPPV in the SWNT/MEHPPV composites on glass plates was estimated by a method described elsewhere [18]. The P-value (0.56) in the SWNT/MEHPPV composites in the presence of magnetic processing (8 T) was larger than that (0.31) in the absence of magnetic processing (0 T). The result strongly indicates that some of the MEHPPV in the SWNT/MEHPPV composites were oriented with the main chain parallel to the magnetic field. Therefore, the anisotropy in the susceptibility of MEHPPV might contribute to the enhancement of the magnitude of the magnetic orientation of the susceptibility of MEHPPV.

Figure 6. Polarized absorption spectra of shortened SWNTs in the presence of NaHCO₃ (0.1 M) on glass plates (a) without (0 T) and (b) with magnetic processing (8 T). Without magnetic processing (0 T), the polarization direction of the light against the longitudinal direction of glass plates is horizontal (0°; red line) or vertical (90°; blue line). With magnetic processing (8 T), the polarization direction of the light against the direction of magnetic field is horizontal H||(0°; red line) or vertical H⊥(90°; blue line). (c) Polarized absorption spectra of shortened SWNTs in the absence of NaHCO₃ on glass plates with magnetic processing (8 T). The polarization direction of the light against the direction of magnetic field is horizontal H||(0°; red line) or vertical H⊥(90°; blue line).
the SWNT/MEHPPV composites. Further investigations are necessary to clarify the role of the MEHPPV in the magnetic orientation of the SWNT/MEHPPV composites.

4. Conclusion

Observations of the AFM images and the polarized absorption spectra of the SWNT/MEHPPV composites or the shortened SWNTs in the absence and the presence of NaHCO$_3$ on substrates (glass plate or mica) revealed that the magnetic orientation of the SWNTs/MEHPPV composites or the SWNTs on substrates (glass plate or mica) could be achieved by applying a strong magnetic field (8 T; horizontal direction). The SWNT/MEHPPV composites or the SWNTs were oriented with the tube axis parallel to the magnetic field. On the basis of a comparison of the SWNT/MEHPPV composites and SWNTs, the magnetic orientation of SWNT/MEHPPV composites is most likely ascribable to the anisotropy in the susceptibility of SWNTs. The present study provided useful information for designing functional nanomaterials consisting of SWNTs or the composites by magnetic processing with a strong magnetic field.

Further studies involving quantitative analysis of the magnetic orientation of the SWNT/MEHPPV composites or the SWNTs in a horizontal magnetic field (8 T) and on the effect of the magnetic orientation of the SWNT/MEHPPV composites on the photoelectrochemical properties of electrodes with the composites are now in progress.

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