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In Plane Orientation of SWCNT Ultrathin Film Fabricated Using a Liquid–Liquid Interface

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Non-chemically treated single-walled carbon nanotubes (SWCNTs) were assembled at a liquid–liquid interface in the shape of an ultrathin film. SWCNTs were dispersed into water phase by aid of sodium dodecyl sulfate (SDS) and were assembled at a hexane-water interface with addition of ethanol. The assembled film was transferred onto a solid substrate at various dipping speeds. Polarized absorption spectra of the transferred film indicated that the SWCNTs aligned with their long axis parallel to the dipping direction when the assembly was transferred at the dipping speed of 50 mm/min.

Keywords Liquid–liquid interface; orientation; single-walled carbon nanotubes

Introduction

Nanomaterials, such as metal and semiconductor nanoparticles, carbon nanotubes, graphene, etc. show unique physical properties which are different from its bulk state. Hierarchical assembly of nanomaterials is the key issue for applying those unique properties to real devices. Several process, such as layer-by-layer assembly, Langmuir-Blodgett (LB) film, and self-assembly have been applied to assemble nanomaterials in a tailor-made manner. We and other groups have applied a liquid-liquid interface to assemble nanomaterial in a two-dimensional manner [1–6]. Recently, we succeeded to fabricate pristine SWCNT ultrathin film using a liquid-liquid interface [7,8]. The assembly showed a closed packed structure with nanometer thickness. The assembling technique required no chemical treatment of SWCNTs, therefore the unique electric properties of SWCNTs were retained in the ultrathin film.

Alignment of CNTs to a required direction is important not only for electric, optoelectronic, and electrochemical devices application, but also for increasing

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mechanical strength in CNT-reinforced sheets. Several processes, such as rubbing, electric field, and magnetic field have been used to uniaxially align CNTs [9]. Kim *et al.* have aligned chemically treated SWCNTs using the LB technique [10]. The SWCNTs are aligned at the dipping direction of a substrate during the transfer of the SWCNT film. The alignment is induced by compression of the film with barrier and water flow generated during the film transfer process. A similar dipping process was used to transfer the pristine SWCNT ultrathin film formed at a liquid-liquid interface. Therefore, it is important to study the effect of a substrate dipping speed to the pristine SWCNT film.

In this paper, SWCNT ultrathin film fabricated at a hexane-water interface was transferred onto a silicon substrate by changing the dipping speed of the substrate and their orientations were studied using polarized UV-vis spectra and scanning electron microscope (SEM). The polarized UV-vis spectra indicate that the SWCNTs aligned with their long axis parallel to the dipping direction of a substrate. It was concluded that the alignment was resulted from a liquid flow, which occurred during the deposition.

Experimental Section

SWCNTs were purchased from Unidym Inc. Sodium dodecyl sulfate (SDS) was obtained from Wako Pure Chemicals Ltd. and was used as received. Ten milligrams of SWCNTs and 100 mg of SDS were dissolved in 10 mL of water and sonicated for 1 h at 38 kHz (As OneCorp.). Then the dispersion was centrifuged at 45,500 $\times$ g for 4 h (CS100GXL; HITACHI KOKI). The supernatant was collected and used as a water phase to fabricate the liquid–liquid interface. The initial concentration of the dispersion was calculated as 147 μg/mL using the extinction coefficient of 0.0286 L/mg cm at 500 nm. Prior to use, a silicon substrate (Polished Wafers; SUMCO Corp.) was washed with alkali detergent, acetone, and methanol. SEM images were captured at an acceleration voltage of 10 kV.

Results and Discussion

Figure 1 shows an optical absorption spectrum of SDS-coated SWCNTs dispersed in water. The absorption spectrum exhibited a series of peaks assigned to the optical transition between van Hove singularities in the valence and conduction bands of various SWCNTs. The broadened peaks are evidence that SWCNTs were not isolated; instead they formed bundles inside the single tubular micelle. The high ratio of SWCNTs against SDS; 10 times higher than the reported procedure [11] may be one reason for the bundled dispersion. It should be mentioned that the dispersion was stable for several weeks. The SDS-coated SWCNT water dispersion was used to prepare ultrathin SWCNT films using a liquid–liquid interface. The film was fabricated by following the reported procedure [8]. Briefly, 10 mL of SWCNTs water dispersion (10 μg/mL) was added to a vessel (20 mm of diameter and 50 mm of height). Then 2 mL of n-hexane was added to the vessel to create a liquid-liquid interface. Finally, 5 vol% of ethanol was added to the vessel. We observed that SWCNTs were assembled at the liquid–liquid interface after addition of ethanol. The SWCNTs assembly at the interface was transferred onto a silicon substrate at the dipping speed of 5 mm/min to 50 mm/min. Orientation of SWCNTs in the ultrathin film was studied using polarized UV-vis absorption spectra. It has been

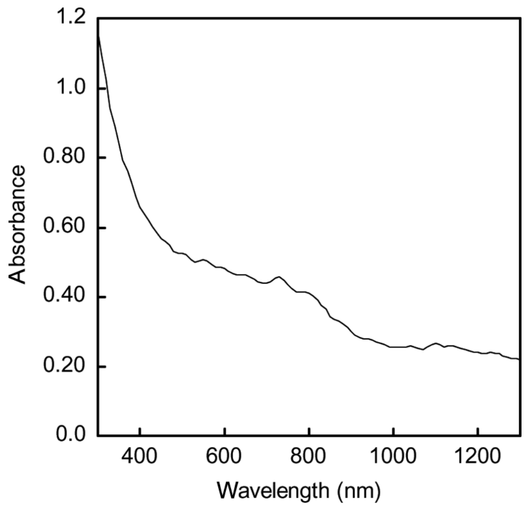

Figure 1. UV–vis–NIR spectrum of SWCNTs in SDS water dispersion.

reported that SWCNTs shows stronger light absorption parallel to the tube length than the tube diameter direction [12,13]. Therefore, measurements of the linear dichroism of the absorption spectra of SWCNT ultrathin films reveal the orientation of the SWCNTs. Figure 2 displays the polarized absorption spectra of the ultrathin SWCNT film deposited onto a quartz substrate with a dipping speed of (a) 5, (b) 10, (c) 25, and (d) 50 mm/min. The polarized absorption spectra of the ultrathin SWCNT films deposited onto a substrate at 5 mm/min and 10 mm/min showed a similar absorption in the light polarized parallel and perpendicular to the dipping direction. Whereas, the polarized absorption spectra of the ultrathin SWCNT films deposited at 25 mm/min and 50 mm/min showed a difference in absorption intensity between the light polarized parallel and perpendicular to the dipping direction. Stronger absorption was observed for the light polarized parallel to the dipping direction than that for the light polarized perpendicular to the dipping direction. A dichroic ratio defined as Abs (parallel to the dipping direction at 555 nm)/Abs (perpendicular to the dipping direction at 555 nm) was calculated to be 1.1 and 1.5 respectively, for the film deposited at the dipping speed of 25 mm/min and 50 mm/min. These polarized absorption spectra indicate that the SWCNTs were aligned at the dipping direction at the higher dipping speed by a flow-induced orientation. The alignment of SWCNTs was confirmed by SEM measurements. The SEM image of SWCNTs transferred at 50 mm/min showed that SWCNTs were aligned at the dipping direction, whereas that of SWCNTs transferred at 5 mm/min showed random orientation of SWCNTs (Fig. 3). The dichroic ratio is smaller than that reported on a SWCNT LB film. In the SWCNT LB film, SWCNTs were partially aligned at the air/water interface due to the compression of the film. However, the SWCNTs assembled at the liquid–liquid interface oriented randomly, because no external force was applied. The liquid flow generated during the film transfer process was the only force to aligned SWCNTs, which resulted in low dichroic ratio. On the other hand, ‘‘pristine’’ SWCNTs can be aligned using the liquid–liquid assembling technique, which has an advantage for electrical and optical device application.

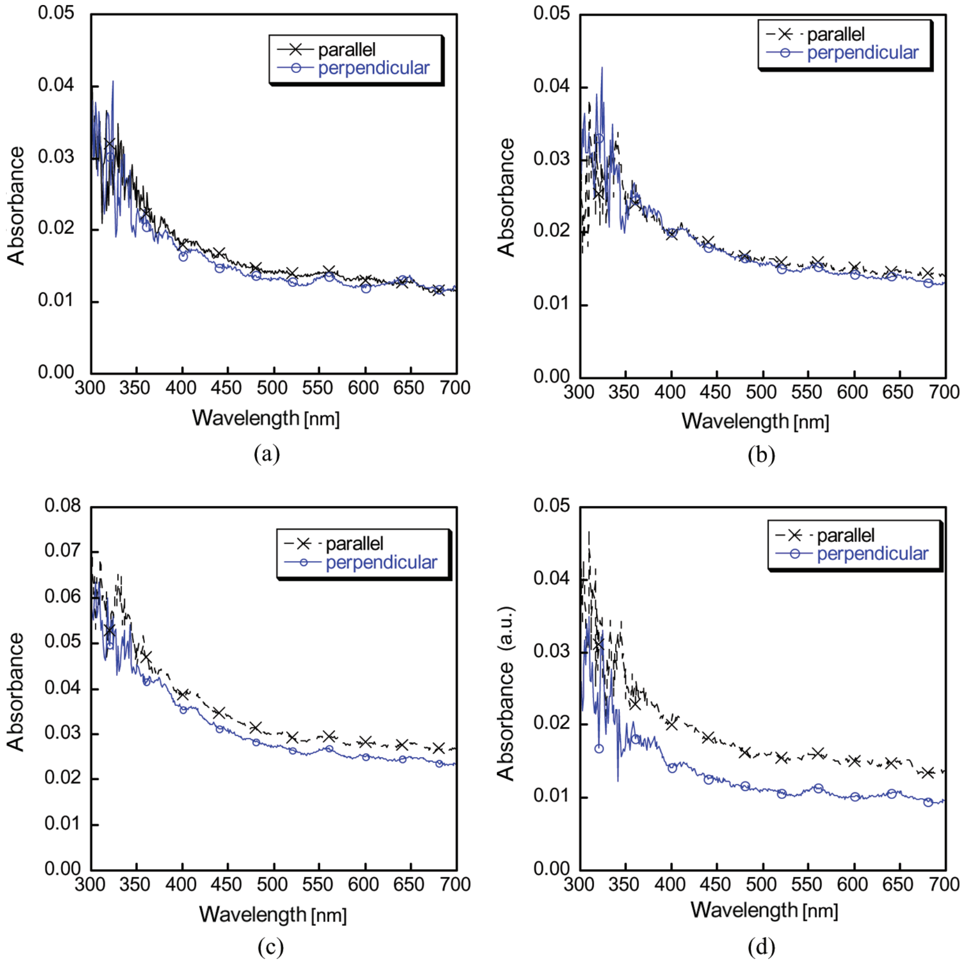

Figure 2. Polarized absorption spectra of the ultrathin SWCNT film deposited at a dipping speed of (a) 5 mm/min, (b) 10 mm/min, (c) 25 mm/min and (d) 50 mm/min.

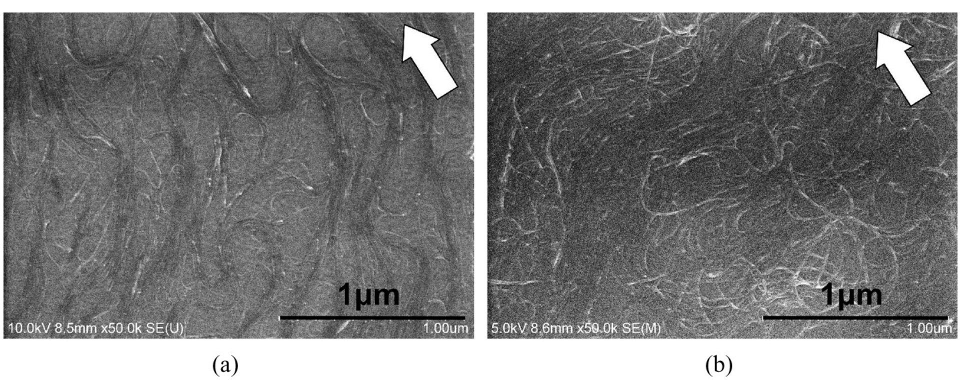

Figure 3. SEM images of the ultrathin SWCNT film deposited onto a silicon substrate at a dipping speed of (a) 50 mm/min and (b) 5 mm/min.

Conclusion

Ultrathin SWCNT films assembled at a liquid-liquid interface were deposited onto solid substrate with changing the dipping speed. Polarized absorption spectra of the ultrathin SWCNT film indicated that SWCNTs were oriented in the dipping direction at high dipping speed (50 mm/min) due to a flow-induced orientation with a dichroic ratio of 1.4. The higher dipping speed and using viscous solution will increase the dichroic ratio.

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