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Anisotropic Carbon Nanotube Films Fabricated from a Lyotropic Liquid-Crystalline Polymer

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Carbon nanotubes (CNTs) are attractive materials in the field of nanotechnology because of their considerable thermal, electrical, mechanical, and optical properties, which arise from the cylindrical π-conjugated system.[1] However, because of the insolubility of CNTs, which is caused by the strong van der Waals interactions, their applications are limited. To overcome this problem, strategic approaches for the homogeneous dispersion of CNTs in host polymers have been undertaken, and successful results have already been reported.[2] To enhance the functional properties of an anisotropic CNT, fabrication of aligned CNT composites is a challenging subject. One of the most efficient approaches to develop aligned CNT materials is the use of liquid crystalline (LC) order and its fluidity.[3]

Recently, the possibility of obtaining nematic phases of acid-functionalized CNTs in water[4] and protonated CNTs in super acids[5] has been shown. However, chemical modifications affect the structure and physical properties of CNTs. On the other hand, a noncovalent functionalization approach is simpler and services CNT composite materials without a change in their intrinsic properties. Therefore, preparation of unfunctionalized CNT/LC composites could be a useful method to enhance their performance. For example, CNTs dispersed in lyotropic LC (LLC) solution can be fabricated as sandwiched LC test cells.[3c] Although fixation of an alignment of CNTs formed from an LC phase is important, preservation of an alignment of CNTs in an LC phase is difficult at ambient temperature, and the sample must be handled in a glass cell because LCs are fluids. Use of a polymer compound exhibiting an LC phase in a solution is one of the most promising approaches to address these problems because polymer solutions form a film after evaporation of solvent, and the order of CNTs is fixed stably at a room temperature. Moreover, previous studies have shown that CNT films possess several advantageous properties like (i) SWCNT have a high transmittance in the visible region, which is an advantage for display applications,[6] and (ii) SWCNTs films can be fabricated at low cost, through an easy process to give structures by solution coating or printing.[7]

Herein, we propose the use of a sulfonated polyaramide, poly(*p*-sulfophenylene-terephthalamide) (PPSA), for the preparation of ordered SWCNT films. PPSA was selected owing to its relevant properties: (i) exhibiting an LLC phase in water,[8] for the alignment of SWCNTs, (ii) amphiphilicity for dispersion of SWCNTs in solution, and (iii) formation of a polymer film for fixation of a CNT order. In previous CNT/LC systems, it was necessary to use several compounds, which separately exhibited the above-mentioned properties. On the other hand, our system satisfies all the above-mentioned conditions in just one compound.

Although polyaramide derivatives have a rigid structure that comprise aromatic and amide groups in the main chain, PPSA dissolves in water and its solution exhibits LLC phase at a concentration greater than the critical concentration of 0.6 wt %. PPSA can play a key role as a surfactant to disperse SWCNTs in the LLC because the sulfonated polyaramide has an amphiphilic structure (Figure 1a). In fact, after sonication in a PPSA/water solution exhibiting an LC phase (left in Figure 1c), we found that SWCNTs formed dispersions that are stable for more than 1 year, and they exhibit an LLC phase (middle and right in Figure 1c). In microscopy images of these LLC samples without analyzer (insets in Figure 1c), bundling was, however, detected at high SWCNT concentration (10 mg of SWCNT/mL), but for 1.0 mg of SWCNT/mL no visible bundles were formed, which indicates homogeneous dispersion of CNTs in the LLC. Solutions containing over ~6 mg of SWCNT/mL became viscous, and they changed to a gel when the solution contained > 10 mg of SWCNTs/mL. The gel formation could be caused by a physical interaction between SWCNTs and PPSA as reported previously in cases such as organic molecules and ionic liquids.[9,10] Although we could not determine the upper limit of dispersion of SWCNT as a result of viscosity of the samples, dispersion of 6 mg of SWCNTs/mL is higher than values reported in previous studies that uses noncovalent functionalization.[11] This is probably because the polymer itself has an amphiphilic structure and is able to act as an efficient surfactant for the dispersion of SWCNTs.

To obtain homogeneously aligned films and evaluate their optical properties, 20 mg of PPSA and 5 mg of SWCNTs were mixed in 1 mL of water and were ultrasonically agitated for 5 h. A small portion of the resultant solution was cast on a glass substrate, and a film was obtained by a bar coater method (Figure 2a). The prepared films appeared transparent (inset in Figure 2b), and the average transmittance of 100 nm thickness of SWCNT/PPSA films over the visible region (400−800 nm) was close to 100%. In the next assessment, we investigated the alignment of the sample films qualitatively by using a polarizing optical microscope (Figure 2c). As viewed through crossed polarizers, transmittance from the homogeneously aligned film was dependent on the rotation angle: that is, when the aligned director was tilted by 45° with respect to the polarizer or analyzer, the transmitted intensity became the highest (right in Figure 2c). On the other hand, the transmitted intensity was lowest at 0° and 90° with respect to analyzer or polarizer as shown in the left panel of Figure 2c. This clearly indicates that the PPSA backbone containing SWCNTs are unidirectionally aligned. We also found that the homogeneous alignment was constant at a room temperature. Moreover, the aligned state of the sample film still preserved its bar coated order when heated to 200 °C for 5 h. To evaluate a qualitative order of the samples, we measured polarized absorption spectra of the film as shown in Figure 3. The parallel absorbance of the transition moment was higher than the perpendicular one. This suggests that the mesogenes of polymer main chain of PPSA are aligned by the barcoater method as shown by polarizing optical microscopy (Figure 2c). Order parameters from absorption spectra (S_{LC}) of the film were evaluated according to a previous study[12]

$$S_{LC} = (R-1)/(R+2) \qquad (1)$$

where R is the dichroic ratio, defined by $R = A_{\|}/A_{\perp}$. From the data in Figure 3, a value of S_{Abs} is between 0.23 and 0.26.

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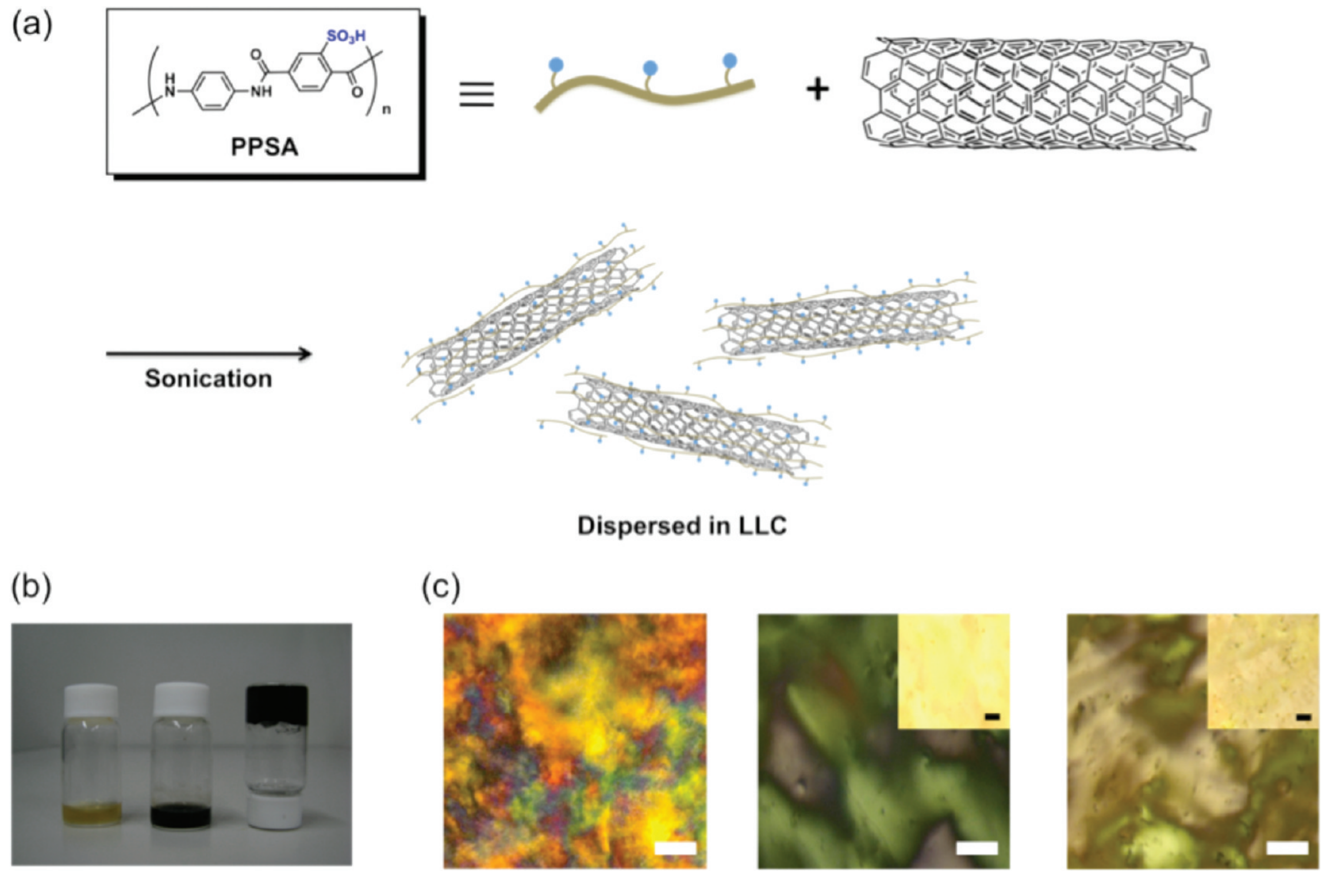

Figure 1. (a) Chemical structure of PPSA and schematic representation of SWCNT dispersion in LLC water. (b) Optical image micrographs of LLC (2.0 wt % of PPSA) with 0, 1.0, and 10 mg of SWCNNT/mL (left to right). (c) Microscopy images between crossed polarizers and without analyzer (insets) of the LLC with 0, 1.0, and 10 mg of SWCNT/mL (left to right). Scale bar: 50 μm.

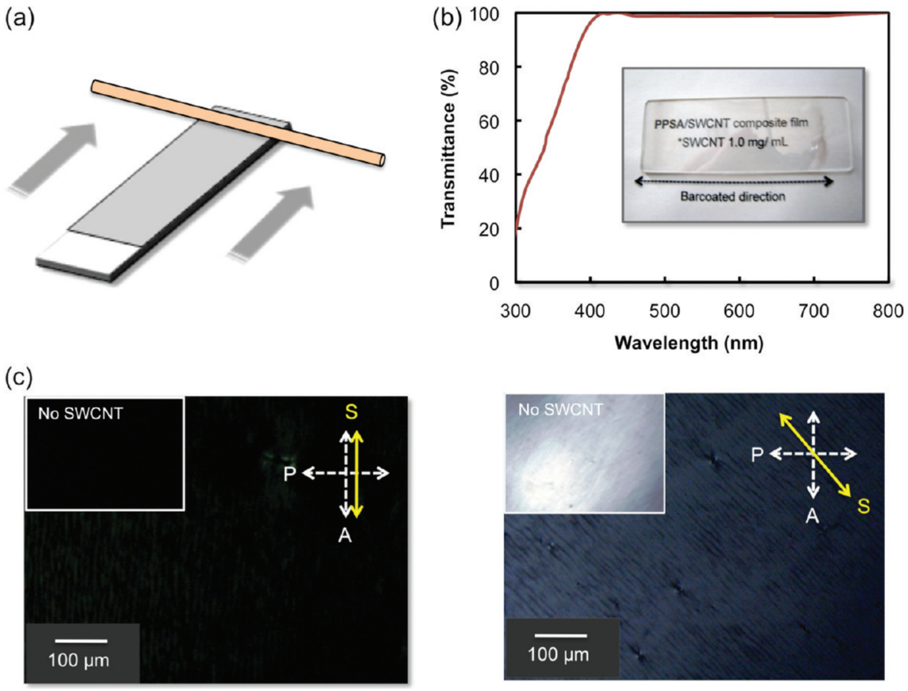

Figure 2. (a) Illustration of the procedure of sample film preparation. (b) Transmittance spectra of the film (2.0 wt % PPSA, 1.0 mg of SWCNT/mL). Inset: optical image of a prepared sample film on a glass substrate. (c) Polarizing optical micrographs of prepared sample films. Left: the direction of sample alignment (*S*) set in parallel to analyzer direction (*A*). Right: *S* set in 45° with respect to polarizer direction (*P*) and *A*. Insets: the same observation in a prepared film (2.0 wt % PPSA) containing no SWCNTs.

In the next trial, we estimated the order parameter of SWCNTs in the sample films. Figure 4a shows a schematic illustration of the optical setup for polarized resonant Raman spectroscopy. The intensities of the SWCNT scattering modes are dependent on the degree of alignment between the CNT axis and the direction of the electric field vector **E** of the exciting laser beam.[13] We concentrated on characteristic scattering bands of SWCNTs, which are the radial breathing mode (RBM) and G-band (Figure 4b). Spectra were recorded at several randomly chosen locations in the sample, and other samples were measured to confirm reproducibility. The Raman mode intensities of $I_{\parallel}$ and $I_{\perp}$ are defined as $\mathbf{E}_{\parallel}$ and $\mathbf{E}_{\perp}$ to the bar coating direction, respectively. In all cases, the SWCNT mode intensity was considerably polarized. The intensity of $I_{\parallel}$ was much larger than that of $I_{\perp}$, which means that the SWCNTs were aligned along the bar coating direction. We can now use eq 1 with the following Raman dichroic ratio (D) to evaluate the order parameter of SWCNTs (S_{SWCNT}).[14]

$$D = I_{\parallel}/I_{\perp} \qquad (2)$$

The data in Figure 4b yielded a S_{SWCNT} value between 0.40 and 0.48, which is higher than S_{LC}. This means that the order of SWCNT alignment is higher than that of template LC alignment. It is known that a long π-conjugated molecular system exhibits a high value of S_{LC} even in the glassy nematic phase, which is a relatively disordered LC phase compared with other LC phases.[15] Therefore, we assume that a SWCNT formed by high anisotropic π-conjugation (aspect ratio: up to1000) shows a larger value of the order parameter than that of the LC template.

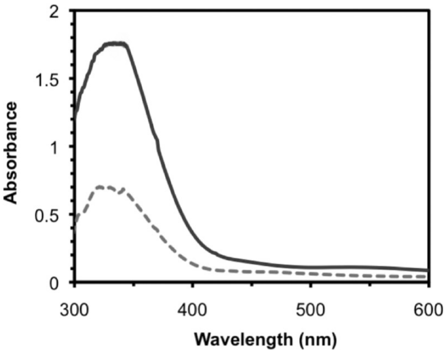

Figure 3. Polarized absorption spectra of the sample film (2.0 wt % PPSA, 1.0 mg of SWCNT/mL). Solid and dotted lines: parallel and perpendicular absorbance to the molecular transition moment, respectively.

In this study, we proposed the possibility of a sulfonated polyaramide exhibiting an LLC phase for the development of a high-performance SWCNT-composite material. The LLC/SWCNT film is prepared from the sample mostly composed of water (97−98%), and the polyaramide is obtained through short and easy synthetic procedures. Therefore, this LLC/SWCNTs system may be an advantage over a purely thermotropic LC/SWCNTs system due to its simple and low-cost sample fabrication. These characteristic properties of the sulfonated polyaramide (LLC in water, amphiphilicity, capacity for film formation, and the simple composite system) enable exploition of high-performance CNT films with broad versatility. We believe that the LLC polymer system can be used to enhance the characteristic properties of other carbon materials such as multiwalled carbon nanotubes, fullerene, graphite, graphene, etc. Based on this system, further investigations are in progress for the development of high thermal conductive and photomechanical materials.

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Supporting Information Available: Experimental procedures and characterization data of polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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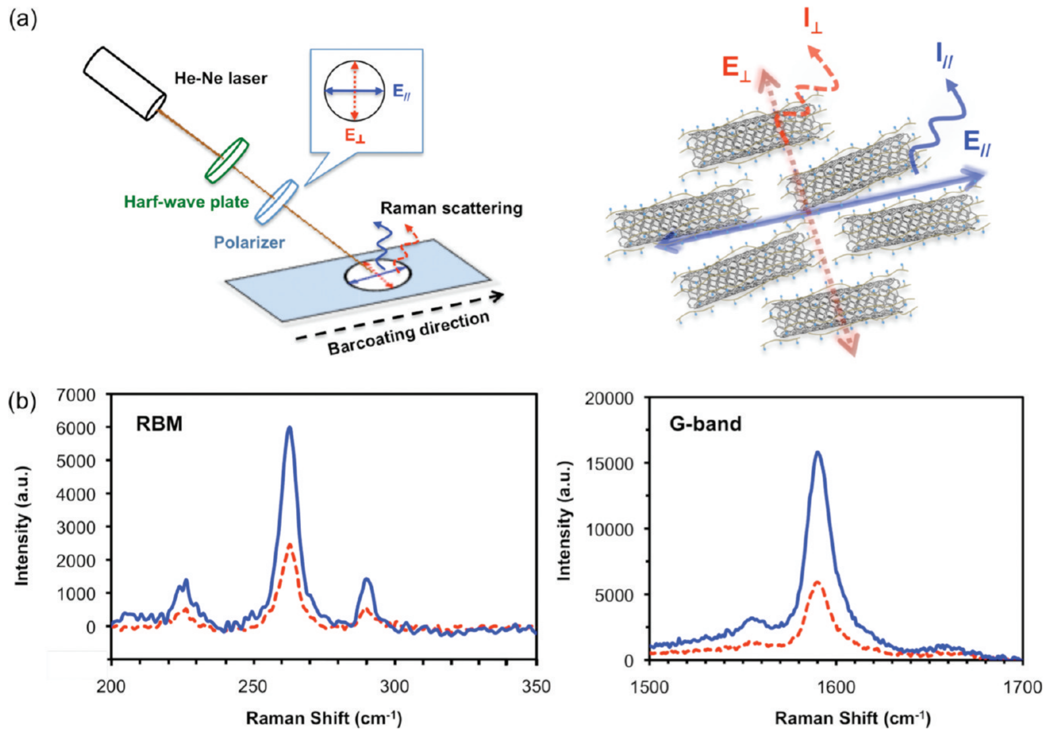

Figure 4. (a) Schematic illustration of an optical setup for measurement of polarized Raman spectroscopy in the sample film. (b) Polarized Raman spectra of the sample film of zoomed area in the range 200−350 nm showing a RBM (left) and the range 1500−1700 nm showing a G-band (right). Solid and dotted lines: Raman mode intensities of $I_{\parallel}$ and $I_{\perp}$, respectively.

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