Optical polarizer made of uniaxially aligned short single-wall carbon nanotubes embedded in a polymer film

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(Received 13 February 2008; published 16 April 2008)

An intrinsic characteristic of carbon nanotubes (CNTs), which are allotropes of carbon, is one-dimensional anisotropy. It is derived from the peculiar geometrical shape of the molecules and is manifested in their electrical, thermal, mechanical, and optical properties. Here, we report an optical polarizer that makes effective use of such anisotropy of CNTs. The polarizer we fabricated is made of uniaxially aligned CNTs embedded in a polymer film. Thanks to the π plasmon-originated broad absorption spectrum and strong optical anisotropy of single-wall CNTs (SWCNTs), the film exhibits a degree of polarization of ~90% with keeping flat transmittance through the spectral region from 350 to 800 nm. In order to efficiently obtain well-aligned CNTs, we used SWCNTs shortened into a length of less than 200 nm. We also observed enhancement of the degree of polarization at the wavelengths of Van Hove singularities.

DOI: 10.1103/PhysRevB.77.153407 PACS number(s): 42.79.Ci, 81.07.De, 82.35.Np

Carbon nanotubes (CNTs) are macromolecules consisting of nanometer-size cylindrical tubes of graphite sheets. Consequently, CNTs exhibit two intrinsic optical properties: black color and anisotropy. Indeed, the basic constituent of CNTs is graphite, which has a strong optical absorption by the π-π^* transition of electrons. Furthermore, the plasma frequency of graphite π electrons is ~7 eV, which causes a strong optical absorption in the visible region, as well as in ultraviolet and infrared regions. Besides these, CNTs show a peculiar geometrical shape, which, in turn, leads to optical anisotropy. In particular, an isolated single-wall CNT (SWCNTs) is considered to have extremely strong optical anisotropy. It was theoretically reported that the optical absorption of single straight SWCNT is completely suppressed by the depolarization effect when the polarization of light is perpendicular to the direction of the axis of the CNT, while for the polarization parallel to the CNT axis, the antenna effect yields a strong absorption.[1] The extinction of resonant Raman scattering, Rayleigh scattering, and photoluminescence emission from an individual SWCNT by the polarization of excitation light are experimental evidences of such optical anisotropy.[2–5] Uniaxially aligned CNTs, such as a bundle of SWCNTs,[6,7] SWCNT forests produced by chemical vapor deposition,[8,9] electrically aligned SWCNTs in solution,[10,11] and a uniaxially stretched polymer/SWCNT composite,[12–15] also exhibit anisotropic optical responses. Since mass-produced high purity SWCNT powder is commercially available recently, such extreme anisotropic absorption within the wide spectral range from ultraviolet to near infrared is attractive for practical optical applications.

We prepared uniaxially aligned SWCNTs embedded in polyvinyl alcohol (PVA) as an optical polarizer [Fig. 1(a)]. The procedure we performed is similar to the technique used for the common iodine-PVA polarizer and is also reported by some groups for obtaining aligned CNTs to study the polarization dependent optical properties of CNTs.[7] 5.5 mg HiPco SWCNTs (CNI, Inc.) were uniformly dispersed in a 14 ml water solution of 1.0% TritonX-100 nonionic surfactant under ultrasonication (Digital Sonifier S-250D Branson) at 20 W for 1 h. The solution was centrifuged in 10 000 g for 20 min, and the supernatant suspension was extracted. 12.5 ml of the CNT suspension was then mixed with 1.5 g of PVA powder (degree of polymerization of 3500; Wako Pure Chemical Industries Ltd.) and exposed under ultrasonication for additional several hours. During the strong sonication, the temperature of the SWCNT/PVA mixture rose close to the glass transition temperature of PVA, which is ~85 °C, whereby the viscosity of PVA significantly dropped and SWCNTs were effectively dispersed in the viscous PVA solution. The SWCNT/PVA mixture was cast on a glass plate and dried out to form a solid film with a thickness of 200–300 μm. A few particles of entangled SWCNTs with the size of a few micrometers were found in the dimensions of 50×50 μm^2 under a transmission optical microscope; otherwise, the film was almost optically homogeneous. The film was peeled off from the glass plate and was cut into a rectangular shape with a length of ~3 cm and a width of ~2 cm. It was then mechanically stretched by applying gentle heat and humidity until the length of the film reached to four times longer than the initial length without crystallization of PVA. The film was left for one day while keeping the stretching tension until the film was fixed. Figure 1(b) is a scanning electron microscope (SEM) image of the surface of the stretched SWCNT/PVA film. The CNTs were extended to form a straight shape in the stretching direction by the mechanical tension. Judging from the width of the lines in the image, the CNTs visualized here are bundled SWCNTs. However, there should be also isolated SWCNTs, which are not possible to be seen because of the lack of the spatial resolution of SEM.

Figures 1(c) and 1(d) show the transmission spectra of the SWCNT/PVA composite film before and after stretching, re-

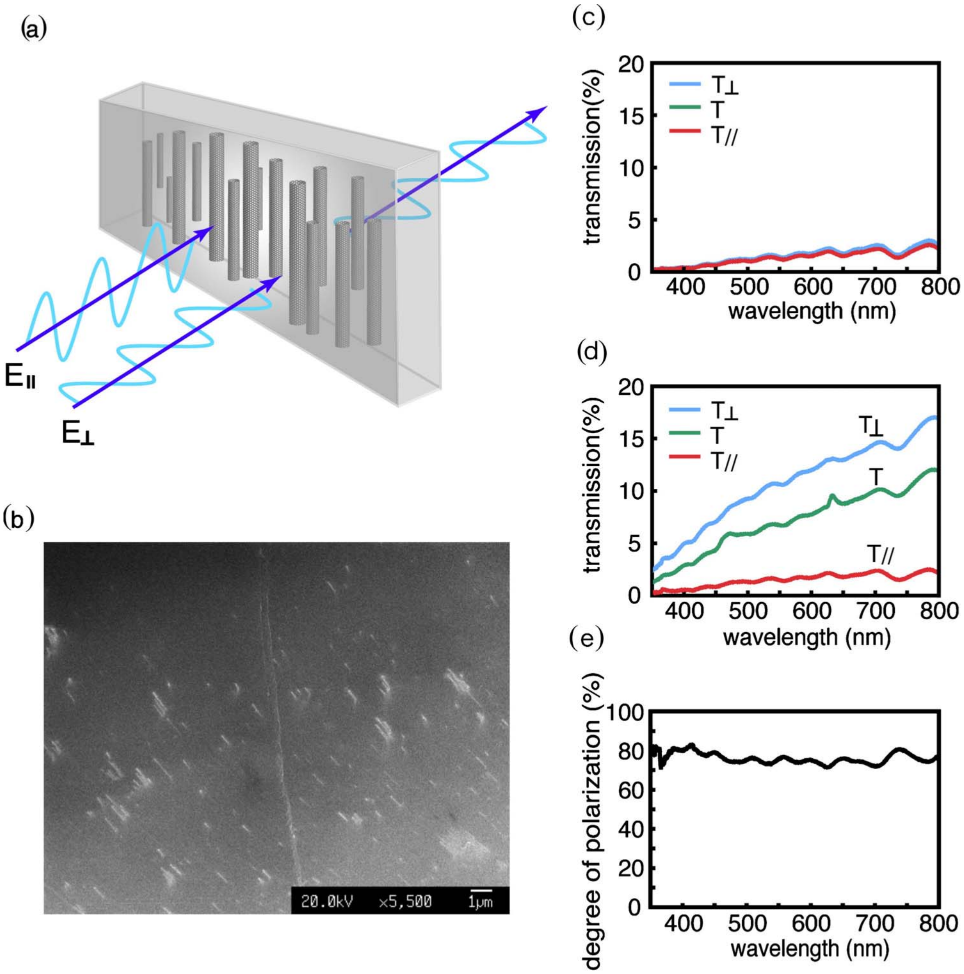

FIG. 1. (Color online) Optical polarizer made of an aligned SWCNT/PVA film. (a) Schematic of the aligned SWCNT/PVA polarizer. (b) A scanning electron microscope image of the surface of the stretched SWCNT/PVA composite film. The white lines in the image are bundled CNTs lying near the surface of the film. It is seen that CNTs are uniaxially extended along the stretching direction of the film. Transmission spectra of the CNT/PVA composite film (c) before stretching and (d) after stretching. $T_{\parallel}(T_{\perp})$ shows the transmittance for light linearly polarized parallel (perpendicular) to the stretching direction. T shows the unpolarized transmission spectrum. (e) The DOP of the light transmitted through the stretched CNT/PVA film.

spectively. The film initially did not show any optical anisotropy, whereas we clearly observed an anisotropic transmission from the stretched SWCNT/PVA film. Figure 1(e) represents the relationship between the degree of polarization[16] (DOP) and the wavelength of the light transmitted through the SWCNT/PVA film. The DOP and unpolarized transmittance at a wavelength of 800 nm are 78% and 12%, respectively. Thanks to the broad absorption spectrum of CNTs originated from graphite π plasmon,[17] the film keeps a DOP of 75%–80% almost constant through spectral region from 800 to 350 nm, which is one of the advantageous properties of a CNT-based optical polarizer. However, unpolarized transmittance gradually decreases as the wavelength of light becomes shorter, which thereby goes toward the π plasmon resonance. In the transmittance spectra shown in Fig. 1, periodic dips are observed. These dips are attributed to the optical absorption peaks by the π-π^* transition of electrons between Van Hove singularities of SWCNTs,[18] and they can be seen when the CNTs are single-wall nanotubes and are debundled to each other in the matrix. It is found in Fig. 1(e) that the DOP was slightly enhanced at these dips seen in transmission spectra of SWCNTs. As known, the quasi-one-dimensional electron system of nanometer-size tubes is the origin of the Van Hove singularity in SWCNTs and, hence, the optical absorption by the electron transition is also governed by the polarization selection rule.[1,19] The experimental result shows that all the dips related to Van Hove singularities both of metallic and semiconducting CNTs contribute to this DOP enhancement.

For an optical polarizer, the ideal values of DOP and unpolarized transmission are 100% and 50%, respectively. In ordinary dye polarizing films or an iodine-PVA optical polarizer, the DOP reaches 90%–95% with unpolarized transmittance of more than 30%. Compared to these values, the CNT/PVA polarizer shown in Fig. 1 does not yet reach a similar quality, although there are some advantages based on the unique properties of CNTs. The most possible reason of the insufficient DOP and simultaneous low transmittance is the imperfection of the alignment of CNTs. Since the length of the SWCNTs produced by the HiPco process sometimes reaches a few micrometers or more, the stretching ratio may not be sufficient to stretch frizzled SWCNTs into a straight-line shape. So, one possible way to improve the DOP is to stretch the film longer. In our experiment, the stretching ratio of the film is limited by four times because of the elasticity of PVA. When the film was stretched more than four times, the film started to tear. Entanglement of CNTs is another possible factor that disturbs the alignment of CNTs. Even though centrifugation was utilized in order to use only isolated CNT suspension, a few amount of bundled CNTs must be still contained in the supernatant suspension or isolated CNTs could rebundle each other when PVA powder was added into the suspension. Indeed, judging from the thickness of the CNTs seen in Fig. 1, many CNTs visualized by

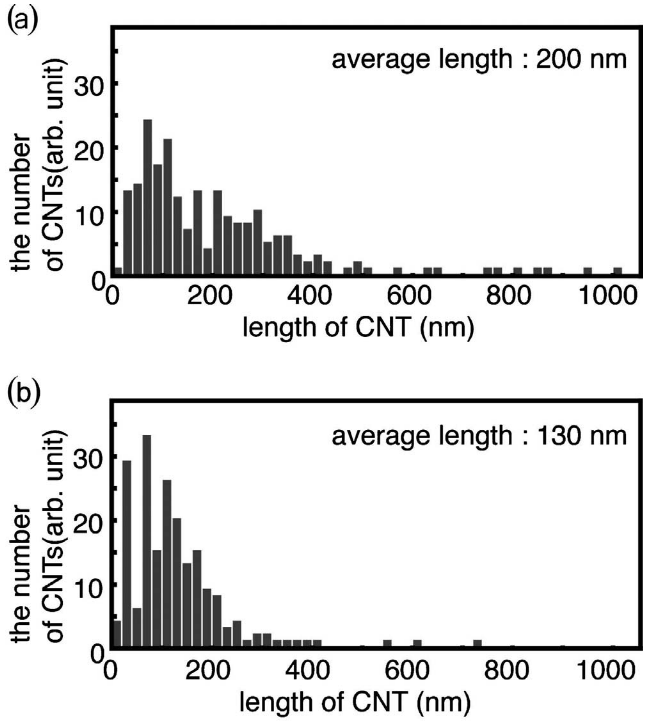

FIG. 2. Distribution histogram of the length of CNTs after ultrasonication treatment in 2,2,3,3-tetrafluoro-1-propanol for (a) 2 h and (b) 8 h. After the treatment, the CNT solution was cast on a glass substrate and dried, then the average length of CNTs was measured through observation by using an atomic force microscope.

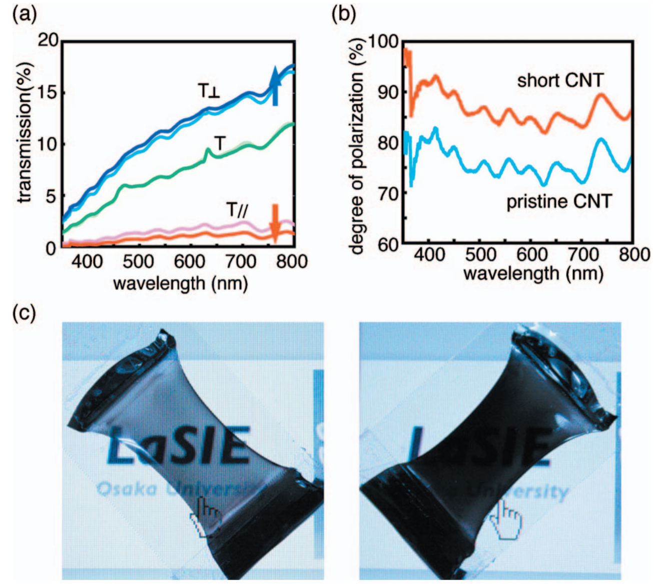

FIG. 3. (Color) Optical property of the polarizer made of a shortened CNT/PVA composite film. (a) Polarized (unpolarized) transmission spectra of the polarizer made of shortened CNT (dense color), as well as the spectra of the pristine CNT/PVA polarizer shown in Fig. 2(b) (light color). (b) The DOPs of the polarizer made of shortened and pristine CNT/PVA composites, in red and blue lines, respectively. (c) Photographs of the stretched CNT/PVA film on a liquid crystal display. The image on the display was only seen when the direction of the carbon nanotube axis is perpendicular to the polarization of light from the display.

SEM observation were almost bundled. An increase in the apparent thickness of CNTs is certainly a cause of the depression of optical anisotropy.[3]

In order to avoid those possible factors, we propose to use shortened SWCNTs. Sano *et al.*[20] experimentally showed that short SWCNTs with a length less than a certain measure, which is called the persistence length, tend to stay straight without bending in solution. Namely, short CNTs are hardly frizzled and entangled with each other. Furthermore, since the CNTs are short, we can expect a better degree of alignment of CNTs with the limited stretching ratio. In our experiment, pristine HiPco SWCNTs were shred into short pieces by means of ultrasonication at 20 W in 2,2,3,3-tetrafluoro-1-propanol. After 8 h sonication, the average length of SWCNTs became 130 nm, a length much less than the persistence length of SWCNTs (Fig. 2). After the process, 2,2,3,3-tetrafluoro-1-propanol was evaporated, and the deposited CNTs were again dispersed into a TritonX-100/water solution. A shortened SWCNT/PVA film was prepared with the aforementioned procedure and stretched with the same stretching ratio as the previous experiment. Figure 3(a) shows the polarized (unpolarized) transmission spectra of the polarizer made of shortened SWCNT/PVA composite. Compared to the spectra of the polarizer made of pristine HiPco SWCNT/PVA, as shown in Fig. 3(b), the DOP of the polarizer of the shortened SWCNT/PVA was improved with similar transmittance at any wavelengths. At the wavelength of 800 nm, the DOP and unpolarized transmission were 86.6% and 12.0%, respectively. We tried to observe the alignment of SWCNTs with a scanning electron microscope but SWCNTs were not visualized from the shortened SWCNT/PVA film. We interpret it as evidence that the CNTs were more debundled and uniformly dispersed compared to the case of pristine HiPco SWCNT/PVA film. Figure 3(c) is a photograph that demonstrates our developed CNT/PVA optical polarizer on a liquid crystal display. When the direction of the polarizer was parallel to the polarization of light, the image on the display was seen through the SWCNT/PVA film, whereas the image disappeared when the film was rotated by 90°. Such a behavior agrees with both the transmission and the DOP previously reported.

Since the large optical anisotropy of CNTs is based on their geometrical shape, we should know the adequate minimum length of CNTs in order to retain their anisotropy. We calculated the relationship between the optical property of the CNT/PVA film and the length of CNTs by using effective medium approximation.[21] In the model, the effective dielectric constant of the SWCNT/PVA composite film is described by the following equation:

$$f\frac{\varepsilon_{\mathrm{CNT}}-\varepsilon_{\mathrm{eff}}}{\varepsilon_{\mathrm{eff}}+L(\varepsilon_{\mathrm{CNT}}-\varepsilon_{\mathrm{eff}})}+(1-f)\frac{\varepsilon_{\mathrm{PVA}}-\varepsilon_{\mathrm{eff}}}{\varepsilon_{\mathrm{eff}}+L(\varepsilon_{\mathrm{PVA}}-\varepsilon_{\mathrm{eff}})}=0. \quad (1)$$

$\varepsilon_{\mathrm{CNT}}$, $\varepsilon_{\mathrm{PVA}}$, $\varepsilon_{\mathrm{eff}}$, and f are the complex dielectric constant of CNTs, complex dielectric constant of PVA, effective dielec-

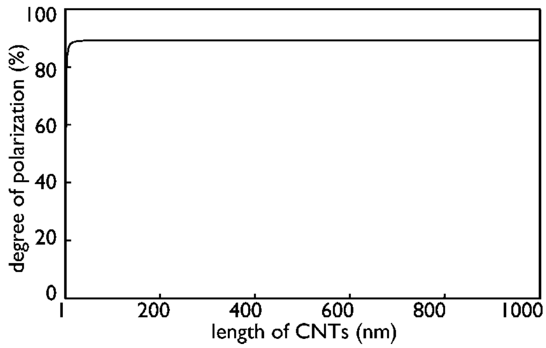

FIG. 4. Relationship between the DOP of SWCNT/PVA polarizer and the length of CNTs calculated by effective medium approximation.

tric constant of the SWCNT/PVA composite film, and volume fraction of CNTs contained in the film, respectively. L is the depolarization factor of CNTs, which is related to the length of CNTs. We assume that the diameter of the CNTs is 1 nm and calculated L with different lengths of CNTs from 1 to 1000 nm.[22] From Eq. (1), we calculated ε_{eff} and the simultaneous DOP of the SWCNT/PVA film at a wavelength of 400 nm. Figure 4 shows the relation of the DOP on the length of CNTs. From 1000 to 100 nm, no evident effect of SNT length on the DOP can be observed. When the length of CNTs scales down to around 50 nm, the DOP significantly drops. This result indicates that about 50 nm is the limit length in order to retain the intrinsic optical anisotropy of CNTs, and we should not reduce the length below this limit.

In conclusion, we fabricated an optical polarizer made of a SWCNT/PVA composite film. We used shortened SWCNTs to improve the alignment of the CNTs in the polymer matrix, leading to the enhancement of the DOP of the polarizer. Thanks to the broad absorption spectrum and strong anisotropy of SWCNTs, the film exhibits a DOP of ~90%, keeping almost constant through the ultraviolet, visible, and near infrared regions. So far, our produced SWCNT/PVA polarizer has a low transmittance compared to the ordinary polarizer; however, taking advantage of the chemical and thermal robustness of CNTs, CNT-based optical polarizer would have a potential to be used for intense light or under severe thermal or chemical circumstances.

This research was supported by CREST, Japan Science and Technology Corporation (JST), and by the Grant-in-Aid for Young Scientists, The Ministry of Education, Culture, Sports, Science and Technology, Japan.

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