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Texture and light-induced anisotropic terahertz properties of free-standing single-walled carbon nanotube films with random networks

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HIGHLIGHTS

- Texture formation was found in single-walled carbon nanotube random networks.
- Modulation of anisotropy in the networks can be done by mechanical stretching.
- The anisotropy can also be enhanced by light illuminating.
- THz spectroscopy offers a way to estimate orientation order of the networks.

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ABSTRACT

We present an anisotropic property investigation of the free-standing single-walled carbon nanotube (SWCNT) random networks by terahertz time-domain spectroscopy (THz-TDS). Strongly anisotropic transmission in the spectral region 0.3–2.5 THz is observed. The experimental observation implies that our pristine SWCNT networks show preferential order in micrometer scale, which are attributed to the formation of the texture pattern. Modulation of this exceptional anisotropy by mechanical stretching and light illuminating indicates that the anisotropic response can be enhanced. The light-induced anisotropic property shows a hyperbolic tangent dependence with the pump power. The results suggest the potential applications and manipulations of SWCNT networks for THz electro-optical and polarized devices.

Single-walled carbon nanotubes (SWCNTs) as intrinsically anisotropic materials have stimulated much attention due to their unique physical properties and their potential applications in electro-optical devices [1]. Spectroscopic techniques employed microwave, far-infrared [2,3], terahertz [4–6], optical absorption/reflection spectroscopy [7–10] and Raman spectroscopy [11,12] have confirmed that the remarkable polarization dependence of the absorption, transmission, and resonant scattering in the in-plane and vertically aligned SWCNT films, or the selectively isolated SWCNTs. These reported results have indicated that the polarized absorption or scattering signal exhibit a maximum when the light is polarized along the nanotube axis, while it is strongly suppressed as the polarized orientation is rotated from parallel to perpendicular. Theoretical studies [11,13] have also corroborated that the anisotropic properties come from the antenna effect due to the one-dimensional characteristic of SWCNT. This means one isolated SWCNT can act as a dipolar antenna polarized along the tube axis and more than one nanotube in aligned films or fibers can behave as a complex multipolar antenna [11]. On the other hand, the electrical transport [14], thermal transport [15], shear stress [16] and charged induced distortion [17] in aligned SWCNT films or in suspensions also show the anisotropic response. With regard to the disordered SWCNT films or networks, few experiments show the anisotropy is relatively high. According to the optical theory [18] with the effective medium assumption [19], a mixture of randomly oriented compositions with SWCNT becomes evidently averaged in all orientations, reducing the anisotropic information that might be obtained by macroscopic probes when the wavelength λ and the unit dimension d satisfy the restriction of $d \ll \lambda$.

In this paper, orientation-dependent measurement by THz time-domain spectroscopy (THz-TDS) reveals that our pristine disordered SWCNT networks grown by chemical vapor deposition technique can show high anisotropy ascribed to the formation of

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texture pattern. When the preferential texture axis and the polarization of THz pulse wave are parallel, the transmission is low. While in the perpendicular orientation, the transmission is high. This exceptional anisotropic response can be enhanced artificially by mechanical stretching and 800 nm light illuminating. The light-induced anisotropic property shows a hyperbolic tangent dependence with the pump power. These indicate that THz-TDS provides a convenient and sensitive measurement for the evaluation of the order degree of SWCNT networks. Furthermore, a sound understanding of the anisotropic properties of the SWCNT networks in THz region is essential for applications of SWCNT networks as polarization-sensitive and electro-optical devices.

In the past decade, many efforts have been contributed to synthesize large-sized SWCNT materials for filter and sensor membranes, electromagnetic shields, field emission displays and so on by easy methods [20]. Our large-sized samples were synthesized by the method of optimum floating chemical vapor deposition technique as described in reference [21]. The area of the pristine large-scale SWCNT non-woven material can reach several tens of square centimeters. These large pieces of SWCNT networks can be handed and manipulated easily. Simple purification including oxidation in air and treatment with concentrated HCl without destroying the networks' compact structure was performed to eliminate impurities in the original SWCNT non-woven material. Scanning electron microscopy (SEM. S-5200) image of the SWCNT networks is shown in Fig. 1 with the scale bar of 300 nm (a), of 500 nm (b), and of 1 μm (c). It is evident that the SWCNT networks are highly entangled with each other, resulting in a highly disordered free-standing films. The diameter of the carbon nanotubes in the bundles is about 1–2 nm and the diameter of the assembled bundles is about 30 nm.

Our home built THz-TDS system is similar to the experimental setup in references [22,23]. Ti-sapphire femtosecond laser (Spectra-Physics Laser Inc.) possesses the physical parameters as follows: a central wavelength of 800 nm, a repetition rate of 82 MHz, a pulse width of 100 fs, and an average power of 0.70 W. The laser pulses are divided into three beams by beam splitters, one beam for generating THz pulse wave using the transient optical rectification effect in GaAs (110), the second beam for probing THz pulse wave by the linear electro-optical effect in ZnTe (110), and the third beam for illuminating samples to demonstrate the light influence. Using polarization detection and changing the motorized delay-line between the generating and probing beams, we can obtain the whole electric component of the THz pulse wave. All the optical elements from generation to detection of THz pulse wave should be encapsulated in a vacuum chamber to eliminate the influence of the water vapor in the air [24]. The free-standing samples are mounted into a metallic sample holder with a central hole of 1 mm diameter. The metallic sample holder can also guarantee the same diffraction condition at the cases with the sample and without the sample. The sample holder is then placed between two parabolic mirrors and can be rotated along the normal direction of the samples. All our experiments are done at the normal incidence. To demonstrate the anisotropic response of the samples, the samples are rotated along the THz wave vector k axis, while we monitor the peak transmission of the THz pulse wave.

Fig. 2(a) presents an angular dependent transmission of the peak of THz pulse wave. This response should come from the projection of the electric field **E** onto the preferred texture axis of the SWCNT networks. It is noted that the SWCNT networks observed in SEM (Fig. 1(a)–(c)) is in a random orientation on the scale of several hundred nanometer. But to our surprise, the sample shows exceptionally anisotropic response in Fig. 2(a) and the ratio of $T_{\perp}/T_{\parallel}$ is as high as 2.5. This value is higher than the results obtained by Jeon et al. [4,25], who aligned SWCNT on a bar coater with a simple mechanical squeezing. According to Ajiki and Ando's theoretical assumption [26,27], the absorption ratio of light polarized parallel versus perpendicular to the tube axis is up to about 20 times for a single carbon nanotube and our result could be reasonable. The difference with Jeon's results would come from two aspects. One is the influence of the substrate (our sample is free-standing), and the other comes from the different sample synthesis and preparation. We also tested our other random networks by controlling carefully the preparation condition and we got the similar results. As the network pattern would show the preferential texture axis, all the individual SWCNT can project onto the

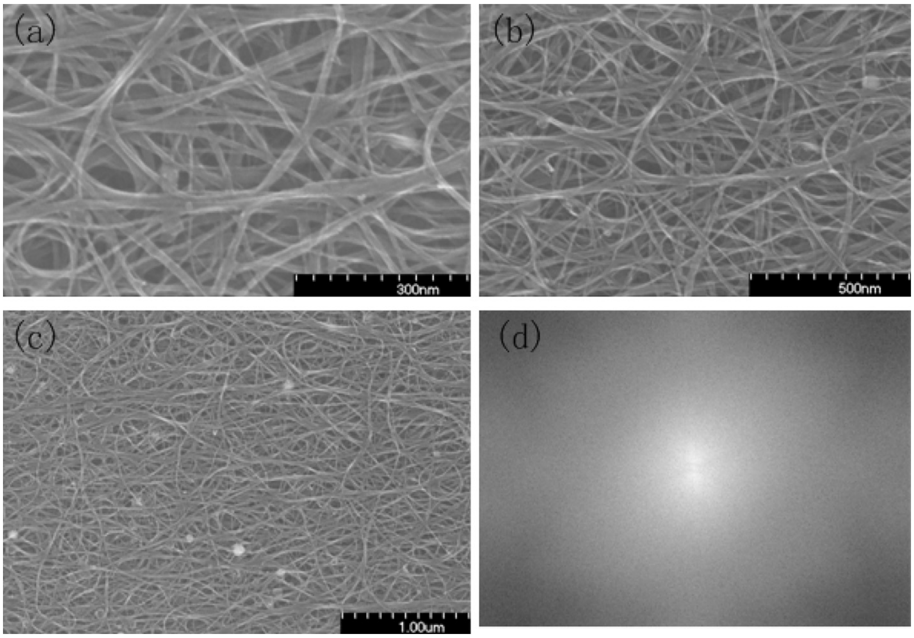

Fig. 1. SEM image of random SWCNT networks with the scale bar of 300 nm (a), scale bar of 500 nm (b), and scale bar of 1 μm (c). (d) Fourier transformation of SEM image of (c) to the moment space, which suggests the texture generation.