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Probing structure and strain transfer in dry-spun carbon nanotube fibers by depth-profiled Raman spectroscopy

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The structural properties of dry-spun carbon nanotube (CNT) fibers were characterized by depth-profiled polarized Raman spectroscopy. Results showed that the twisting cannot be fully transferred through the whole fiber and the CNTs within fibers possess non-uniform alignments in radial direction. Effective twisting depth was determined from the residue strain distribution within fibers. Larger surface twisting angles can result in higher residue strain, better alignment degree, and deeper twisting depth. This research suggests a balance should be built between the enhancement of CNT interactions and the increase of defect density to obtain high-performance fibers. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4815926>]

Recent emergence of carbon nanotube (CNT) fibers has triggered a new research interest for CNT materials.^{1,2} These continuous CNT fibers are composed of a large number of well aligned individual CNTs or their small bundles,^{3,4} shown a strength of 0.1–10 GPa,⁵ which is far smaller than that of individual CNTs.⁶ Generally, this was attributed to the weak tube interactions between CNTs within the fibers. Up till now, considerable efforts have been reported to enhance the tube interactions by using long and well-aligned CNT arrays,⁷ improved spinning methods,^{8,9} and post-spinning treatments.^{10,11} Among those post-spinning treatments, twisting is one of the most frequently used methods to densify the CNT fibers and enhance their tensile strength.^{11–14} Like cotton spinning, twisting treatments can decrease the diameter of the fibers, enhance the intertube interactions, and thus greatly improve their tensile properties. But at the same time, twisting will change the CNT alignment, indicated by a surface twisting angle on the fiber surface. This formed angle usually weakens the fibers' mechanical behaviours,^{13–15} and the weakening effect becomes more serious when the twisting is not fully transferred through the whole fiber. Thus, twisting treatments will inevitably introduce non-uniform distribution of mechanical strain and/or CNT alignment degree in radial direction,¹⁶ which could greatly affect the structural characteristic of the fiber.^{17,18} Therefore, it is very important and instructive to conduct a depth-profiled analysis on the structure of the fibers along their radial direction, and then study the influence of such structural changes on fibers' mechanical properties.

Raman spectroscopy, as a nondestructive and useful technique, was frequently used to study the structural properties of CNT fibers.^{17–20} When CNTs are mechanical strained or stressed, Raman peaks will shift their positions according to the local strain or stress. Moreover, Polarized Raman

signals are particularly sensitive to the CNT alignment, and can be used for depth-profiled measurements to study the cross-section distribution of the samples.^{21,22} In this work, a combination of depth-profiled and polarized Raman measurements has been employed to investigate the radial structure of CNT fibers. The results indicated that the twisting introduce non-uniform CNT alignment and non-uniform residue strain in radial direction. Effective twisting depth has been used to describe the twisting transfer in a fiber. Also, it was found that the distributions of the alignment and the residue strain changed according to the surface twisting angle.

CNT fibers used in this study were spun from vertically aligned CNT arrays using a micro-spindle mounted on a motor with an adjustable rotation speed (120–350 rpm). The detailed information of array growth and fiber spinning can be reviewed in our previous work.^{23–26} In this work, five types of samples with different twisting were prepared for the study of depth-profiled polarized Raman spectroscopy. And the Raman behaviours were studied on a Renishaw inVia confocal Raman microscope with the 632.8 nm line of a He-Ne laser under a high confocality mode. Moreover, the morphologies of the prepared fibers were characterized by a JOEL JSM-7600F scanning electron microscope (SEM).

It is demonstrated in our previous work that twisting treatments can push the CNTs to contact with each other more closely, enhance the van der Waals forces and friction, and thus improve the load transfer between the CNTs.¹⁶ Here, to further determine the structural properties of our fibers, we have conducted a series of depth-profiled polarized Raman measurements on the twisted CNT fibers, as schematically illuminated in Fig. 1. The laser polarization direction is parallel to x-axis of Raman measuring platform. Before the measurements, the samples were placed on an x-y Raman measuring platform. Then, all Raman spectra were taken at high confocal mode with the minimum z interval step size (0.1 μm). The Raman intensity is proportional to $\frac{p^2}{p^2+z^2} \times e^{-2\alpha z}$, where z is the focus depth, p is the in-depth probe response parameter, which tends to infinity for an

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FIG. 1. 3D-schematic description of depth-profiled Raman measurements. Left inset: normalized intensity plotted against the angle between the polarization direction of the laser light and the pristine CNT fiber, compared to values calculated from $I = I_0 \cos^4 \theta$ (red line). Right inset: depth-series of Raman spectra from the surface to the core of the fiber.

unfocused beam, and α is the absorption coefficient of the material at the incident wavelength.^{27,28} This technique has combined the advantages of both polarized and depth-profiled Raman spectroscopy. The left inset in Fig. 1 shows the polarization behavior of the untwisted CNT fibers measured at 633 nm, which is in good agreement with that predicted by $I = I_0 \cos^4 \theta$, where θ is the rotation angle during the measurement. The right inset in Fig. 1 presents a series of depth-profiled Raman spectra. It can be found that the intensities of Raman bands decreased with the increased focus depth to the fiber core, which agrees with the above statements.

At the same time, the detail information (such as peak position, peak intensity, and peak width) can be obtained by fitting those Raman bands (D, G, and G') using a Lorentzian profile, as shown in Fig. 2(a). The red and green lines are obtained from Lorentzian fitting, and the inset table is the fitting results. The D band of CNTs locates at 1327 cm^{-1} , the G' band of CNTs locates at 2646 cm^{-1} , and the Raman band near 1600 cm^{-1} could be resolved into two modes at 1580 cm^{-1} (G band) and 1612 cm^{-1} (D' band). Normally, D' bands were caused by the collapsed structure in the twisted CNT fibers.^{12,18,29}

Twisting treatments usually result in the polarization angle offset in the twisted CNT fibers.¹⁶ As shown in the inset table of Fig. 2(b), it can be found that the polarization angle offset first decreases with the increasing focus depth, and reaches its minimum value of 7.5° at focus depth of $-3 \mu\text{m}$. Further increasing focus depth, the polarization angle will increase and reach 10° at focus depth of $-4.0 \mu\text{m}$. These results confirm that the twisted fiber consists of different alignments with a large twisting angle at the surface and a small twisting angle near the core of the fibers. Thus, the polarization angle is small when the focus is close to the core, because CNTs in the core part contribute more to Raman signal. While the focus is near to the surface of the CNT fiber, the polarization angle will increase because the surface CNTs contribute more to Raman signal.

On the other hand, it can be seen that the distribution of the measured depth profile of angle offset is not centered as that of the twisted fibers. This should be due to the co-action of surface and inner CNTs, although the transmittance of the stretched CNT films can reach as high as above 80% ($0.55 \mu\text{m}$).^{30,31} To explain this point, here we can image a

simple core-shell structure for our twisted fiber,¹⁶ in which the surface angle offset is noted as θ_s , and the inner angle offset as 0. When moving the focus point towards the center of the fiber, the more and more contribution from inner CNTs can be obtained, assumed that the transmittance of CNT fiber is 80%, then the angle offset θ can be described as $\arctan(\frac{\sin 2\theta_s}{\cos 2\theta_s + 0.8x\% / (1-x\%)})$, where x is the content of the total light energy acted on the inner CNTs. It is seen that θ will monotonously decrease with the increasing x . Once the focus move over the center and enter the surface layer region, x will decrease and angle offset θ will restore. So, for this

FIG. 2. (a) Typical Raman spectra of a twisted CNT fiber. (b) Depth profiles of CNT alignment degree for the twisted fiber. Inset table in (a): fitting results of Raman bands (D, G, D', and G') using a Lorentzian profile; inset table in (b): Polarization angle offset of the twisted CNT fiber under different focus depths.

case, the minimum angle offset will not appear at the center of the fibers.

Generally, this type of variation in polarization angle is associated with the microscopic alignment change in the twisted CNT fiber, and the degree of polarization $P = (I_{\max} - I_{\min}) / (I_{\max} + I_{\min})$ was often used to evaluate the alignment degree of the CNT macro-architecture.¹ The intensities $I_{\max}$ and $I_{\min}$ used here and thereafter are integrated area intensities, similarly listed in the inset of Fig. 2(a). If there exist a small angle bias Δ between polarization direction and real CNT alignment, the P value will change to be $1 - \frac{2}{I_{\max} \cos^4 \Delta / I_{\min} + 1}$, and P value will decrease with the increasing $|\Delta|$.¹⁶ Thus, to obtain a real revaluation of the CNT alignment in the twisted fibers, a series of depth-profile measurements were conducted. Here, $I_{\max}$ and $I_{\min}$ values were measured based on the depth profile of polarization angle offset shown in the inset table of Fig. 2(b). For instance, to obtain the P value at the focus depth of $-2 \mu\text{m}$, first the measured fiber was rotated to the polarization angle offset of -10° and the focus of the laser was set to $-2 \mu\text{m}$, then $I_{\max}$ and $I_{\min}$ values can be exactly obtained at rotation angle of -10° and 80° , respectively. As shown in Fig. 2(b), the P value decreases from 0.25 to about 0.15 with the focus depth increasing from $0 \mu\text{m}$ to $-2.0 \mu\text{m}$, and then increase up to 0.24 at the focus depth of $-4.0 \mu\text{m}$, i.e., the twisted fiber possess a non-uniform alignment in radial. The surface of CNT fiber has a higher alignment degree due to the twisting, and the core of the fiber possesses a relative lower alignment degree, which is mainly associated with the quality of CNT array.¹⁷ These above results on polarization and depth profile research suggest that the twisting has reinforced CNT fibers by decreasing the fiber diameter and improved the surface CNT alignment degree. However, this twisting was not effectively transferred to all individual CNTs, thus resulting in a non-uniform alignment distribution in radial.

Twisting treatments can not only enhance the interaction between CNTs, but also left residue strain inside the fiber. Fig. 3(a) shows the typical depth profile of I_D/I_G ratio of the twisted fiber. It can be seen that from the surface to the core of the fibers, the values of I_D/I_G ratio increase first and reach its maximum value at the focus depth of about $-1 \mu\text{m}$; when exceeding this depth to the core of the fiber, the values decreased quickly. This trend indicates that there forms a non-uniform distribution of defect density in radial direction.^{19,32}

The collapsed structures can easily form during the twisting process. Here, the intensity ratio of D' to G ($I_{D'}/I_G$) was used to describe the content of the collapsed structure in the fibers. Fig. 3(b) shows the dependence of $I_{D'}/I_G$ ratio on the focus depth. From the surface to focus depth of $-1 \mu\text{m}$, it is found that the ratio value increases with depth, and reaches its maximum value at $-1 \mu\text{m}$. When further increasing focus depth from $-1 \mu\text{m}$ to the core of the fiber (about $-2 \mu\text{m}$), the ratio value decreases with depth. This change trend suggests that the highest content of the collapsed structures appears at $-1 \mu\text{m}$ below the surface of the fiber, consistent with the result of I_D/I_G ratio.

The position shifts of G , D' , and G' bands are also monitored and shown in Fig. 3(c). The positions of G , D' , and G' bands were obtained by fitting the Raman spectra using a Lorentzian profile. The peak shifts of G , D' , and G' Raman modes show a reverse change trend to the depth profile of I_D/I_G and $I_{D'}/I_G$ ratios. The biggest downshifts occur at the focus depth of $-1.0 \mu\text{m}$. The downshifts of the peak positions arise from the weakening of the carbon-carbon bonds as a result of the elongated inter-atomic distance during the twisting process.^{17,33} Combining the analysis from the depth profile of I_D/I_G and $I_{D'}/I_G$ ratios, one can imagine that the CNT fiber consist of a surface twisting layer and a bound core, and the special depth in sample of about $-1 \mu\text{m}$ is the effective thickness of surface twisting layer, here defined as effective twisting depth.

FIG. 3. Depth profiles of (a) I_D/I_G ratios, (b) $I_{D'}/I_G$ ratio, and (c) Raman peak shifts.

FIG. 4. Dependence of depth profile of (a) I_D/I_G ratios and (b) peak positions on rotation angles for the twisted fibers; (c) full depth profile of I_D/I_G ratio ($0 \sim -4 \mu\text{m}$). Inset in (c): schematic description of residue strain distribution in a spun CNT fiber.

In order to investigate the effect of rotation angle on the Raman results, Raman depth profile measurements of the twisted CNT fiber were conducted at different rotation angles, i.e., -20° , -15° , -10° , 10° , and 40° . Fig. 4(a) shows the dependence of depth profile of I_D/I_G ratios on rotation angles, and Fig. 4(b) shows the dependence of Raman peak positions of G' band on the rotation angle. It can be seen that there is little difference for the five rotation angles, and the change tendencies appear to be independent of rotation angle, suggesting that our observations are resulted from structure change. The maximum values of I_D/I_G ratios and peak shifts occur at the same focus depth of $-1.0 \mu\text{m}$, indicating an effective twisting depth of $\sim 1.0 \mu\text{m}$.

We use the distribution of I_D/I_G to reconstruct the residue strain in Fig. 4(c): the highest defect density (as well as residue strain) is located at -1 and $-3 \mu\text{m}$ below the fiber surface (for a fiber with a diameter of about $4 \mu\text{m}$). One can easily imagine that, during the twisting process, the twisting is transferred from the surface to the core of the fiber, and the maximum strain should occur at the fiber surface. However, the introduced strain in the outmost surface CNT layer will be slightly released through CNT sliding, leaving the maximum residue strain (and defect density) below the fiber surface.

Since twisting can change the mechanical performance of the fibers,^{11–13,18} it is necessary to investigate the twisting

FIG. 5. Dependence of (a) maximum I_D/I_G ratio, (b) maximum alignment degree, (c) percent twisting depth, and (d) maximum peak shift on twisting angle for the CNT fibers with different twisting angles. Inset in (a) is a schematic map of the twisted fiber, which consist of a twisting layer and a bound core.

distributions change according to surface twisting angle. Fig. 5(a) shows the dependence of I_D/I_G ratios on surface twisting angle of the fibers. As illuminated in the inset of Fig. 5(a), θ_s is the surface twisting angle of the fibers. The maximum values in the depth profile of I_D/I_G ratio monotonously increase with the surface twisting angle. Similar tendency can also be observed from the maximum alignment degree, as shown in Fig. 5(b). It can be found that the maximum alignment degree increases with twisting angles, but saturates at its limit value of about 0.275.

The effective twisting depth is also compared at various surface twisting angles. Since these fibers show different diameters under different twisting, we use percent twisting depth (defined as the percent ratio of twisting depth to the diameter of the fiber) to study the twisting effect. As summarized in Fig. 5(c), the percent twisting depth increases from 7% to 30% with the increasing twisting angle. Similar phenomenon can also be observed from the peak shifts shown in Fig. 5(d). It can be seen that the maximum peak shift increased with twisting angle increasing, indicating that residue strain in the fiber increases with the twisting. These findings may provide an instructive insight on the improvement of fiber performance.

In summary, depth-profiled Raman spectroscopy was employed to investigate the structural properties of dry-spun CNT fibers. The results indicate that a twisted fiber consists of non-uniform CNT alignments in radial direction. The maximum I_D/I_G ratios, peak shifts, I_D/I_G ratios appear at the twisting depth of the fibers. These results imply that the formation of twisting layers could be associated with the residue strain left in the fibers after the spinning process, which also reflect the distribution of the twisting transfer during the process. I_D/I_G ratio and peak position distributions appear to be independent of rotation angles, indicating that the twisting depth is an intrinsic quantity for a dry-spun CNT fiber. The monotonous increases of maximum I_D/I_G ratios, alignment degree, percent twisting depth, and peak shifts according to the surface twisting angle suggest that suitable twisting would benefit for a high-quality CNT fiber. This research would demonstrate a good strategy for quantitatively studying the CNT fibers.

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¹K. Jiang, Q. Li, and S. Fan, *Nature* **419**, 801 (2002).

²R. H. Baughman, A. A. Zakhidov, and W. A. de Heer, *Science* **297**, 787 (2002).

- ³M. Zhang, S. Fang, A. A. Zakhidov, S. B. Lee, A. E. Aliev, C. D. Williams, K. R. Atkinson, and R. H. Baughman, *Science* **309**, 1215 (2005).
- ⁴K. Liu, Y. Sun, P. Liu, J. Wang, Q. Li, S. Fan, and K. Jiang, *Nanotechnology* **20**, 335705 (2009).
- ⁵K. Koziol, J. Vilatela, A. Moissala, M. Motta, P. Cuniff, M. Sennett, and A. Windle, *Science* **318**, 1892 (2007).
- ⁶B. G. Demczyk, Y. M. Wang, J. Cumings, M. Hetman, W. Han, A. Zettl, and R. O. Ritchie, *Mater. Sci. Eng., A* **334**, 173 (2002).
- ⁷K. Jiang, J. Wang, Q. Li, L. Liu, C. Liu, and S. Fan, *Adv. Mater.* **23**, 1154 (2011).
- ⁸M. Motta, Y. Li, I. Kinloch, and A. Windle, *Nano Lett.* **5**, 1529 (2005).
- ⁹C. D. Tran, W. Humphries, S. M. Smith, C. Huynh, and S. Lucas, *Carbon* **47**, 2662 (2009).
- ¹⁰A. Kis, G. Csanyi, J. P. Salvetat, T. N. Lee, E. Couteau, A. J. Kulik, W. Benoit, J. Brugger, and L. Forro, *Nature Mater.* **3**, 153 (2004).
- ¹¹T. W. Cheng and W. K. Hsu, *Appl. Phys. Lett.* **90**, 123102 (2007).
- ¹²X. Zhang and Q. Li, *ACS Nano* **4**, 312 (2010).
- ¹³X. Zhang, Q. Li, Y. Tu, Y. Li, J. Y. Coulter, L. Zheng, Y. Zhao, Q. Jia, D. E. Peterson, and Y. T. Zhu, *Small* **3**, 244 (2007).
- ¹⁴X. Zhang, Q. Li, T. G. Holesinger, P. N. Arendt, J. Huang, P. D. Kirven, T. G. Clapp, R. F. DePaula, X. Liao, Y. Zhao, L. Zheng, D. E. Peterson, and Y. Zhu, *Adv. Mater.* **19**, 4198 (2007).
- ¹⁵Q. W. Li, X. F. Zhang, R. F. DePaula, L. X. Zheng, Y. H. Zhao, L. Stan, T. G. Holesinger, P. N. Arendt, D. E. Peterson, and Y. T. Zhu, *Adv. Mater.* **18**, 3160 (2006).
- ¹⁶J. Zhou, G. Sun, Z. Zhan, J. An, Y. Zhang, Y. Zhang, and L. Zheng, *J. Raman Spectrosc.* **43**, 1221 (2012).
- ¹⁷W. Ma, L. Liu, R. Yang, T. Zhang, Z. Zhang, L. Song, Y. Ren, J. Shen, Z. Niu, W. Zhou, and S. Xie, *Adv. Mater.* **21**, 603 (2009).
- ¹⁸J. Zhao, X. Zhang, J. Di, G. Xu, X. Yang, X. Liu, Z. Yong, M. Chen, and Q. Li, *Small* **6**, 2612 (2010).
- ¹⁹J. J. Vilatela, L. Deng, I. A. Kinloch, R. J. Young, and A. H. Windle, *Carbon* **49**, 4149 (2011).
- ²⁰H. H. Gommans, J. W. Alldredge, H. Tashiro, J. Park, J. Magnuson, and A. G. Rinzier, *J. Appl. Phys.* **88**, 2509 (2000).
- ²¹R. Takei, H. Tanino, S. Chichibu, and H. Nakanishi, *J. Appl. Phys.* **79**, 2793 (1996).
- ²²J. Moreno, F. Agulló-Rueda, E. Montoya, M. Marcos, J. González-Velasco, R. Guerrero-Lemus, and J. Martínez-Duart, *Appl. Phys. Lett.* **71**, 2166 (1997).
- ²³L. Zheng, G. Sun, and Z. Zhan, *Small* **6**, 132 (2010).
- ²⁴Z. Y. Zhan, Y. N. Zhang, G. Z. Sun, L. X. Zheng, and K. Liao, *Appl. Surf. Sci.* **257**, 7704 (2011).
- ²⁵G. Sun, L. Zheng, J. Zhou, Y. Zhang, Z. Zhan, and J. H. L. Pang, *Int. J. Plast.* **40**, 56 (2013).
- ²⁶Y. Zhang, L. Zheng, G. Sun, Z. Zhan, and K. Liao, *Carbon* **50**, 2887 (2012).
- ²⁷A. Atkinson and S. C. Jain, *J. Raman Spectrosc.* **30**, 885 (1999).
- ²⁸G. Pezzotti, *Phys. Status Solidi A* **208**, 976 (2011).
- ²⁹J. A. Elliott, J. K. W. Sandler, A. H. Windle, R. J. Young, and M. S. P. Shaffer, *Phys. Rev. Lett.* **92**, 095501 (2004).
- ³⁰C. Feng, K. Liu, J.-S. Wu, L. Liu, J.-S. Cheng, Y. Zhang, Y. Sun, Q. Li, S. Fan, and K. Jiang, *Adv. Funct. Mater.* **20**, 885 (2010).
- ³¹L. Xiao, Z. Chen, C. Feng, L. Liu, Z.-Q. Bai, Y. Wang, L. Qian, Y. Zhang, Q. Li, K. Jiang, and S. Fan, *Nano Lett.* **8**, 4539 (2008).
- ³²J. J. Vilatela, J. A. Elliott, and A. H. Windle, *ACS Nano* **5**, 1921 (2011).
- ³³C. A. Cooper, R. J. Young, and M. Halsall, *Composites, Part A* **32**, 401 (2001).