Carbon nanotube yarns with high tensile strength made by a twisting and shrinking method

To cite this article: Kai Liu *et al* 2010 *Nanotechnology* **21** 045708

Nanotechnology **21** (2010) 045708 (7pp) doi:10.1088/0957-4484/21/4/045708

Carbon nanotube yarns with high tensile strength made by a twisting and shrinking method

Kai Liu[1,2], Yinghui Sun[1], Ruifeng Zhou[1], Hanyu Zhu[1], Jiaping Wang[1], Liang Liu[1], Shoushan Fan[1] and Kaili Jiang[1]

[1] Department of Physics and Tsinghua-Foxconn Nanotechnology Research Center, Tsinghua University, Beijing 100084, People's Republic of China
[2] Department of Chemistry, Tsinghua University, Beijing 100084, People's Republic of China

E-mail: jpwang@tsinghua.edu.cn and JiangKL@tsinghua.edu.cn

Received 19 October 2009, in final form 23 November 2009
Published 16 December 2009
Online at stacks.iop.org/Nano/21/045708

Abstract

We report a simple and continuous spinning method that combines twisting and shrinking processes to produce carbon nanotube yarns. In this method, a yarn freshly spun from a super-aligned carbon nanotube array is first twisted and then passes through a volatile solvent for shrinking. The as-produced yarn consists of densely packed carbon nanotubes, and thus has a tensile strength up to about 1 GPa. The tensile strength depends on the diameter and the twisting angle of the yarn. Different kinds of solvents, such as water, ethanol, and acetone, are used to shrink the twisted yarns, and acetone shows the best shrinking effect. The origin of the solvent shrinking effect is investigated. Our method is favorable for continuous mass production of high strength carbon nanotube yarns with a wide range of diameters, especially ultra-thin yarns.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Carbon nanotube (CNT) is an attractive one-dimensional nanomaterial with extremely high tensile strength and Young's modulus [1–3]. However, a problem remains concerning how to make macroscale CNT yarns that can fully utilize the excellent mechanical properties of microscale CNT. The early fabrication of CNT yarns was based on wet spinning methods [4–8], which required dispersing CNTs in a solution for further spinning process. The chemical dispersing process generally led to a low usage of CNTs, and the spun yarn usually contained surfactant or polymer molecules which reduced its thermal and electrical conductivity. To avoid these disadvantages, dry spinning methods were developed to prepare CNT yarns composed of pure CNTs by direct synthesis [9, 10], spinning CNTs during the growth process [11, 12], twisting as-grown CNT films [13, 14], or spinning CNTs from as-grown super-aligned CNT (SACNT) arrays [15–23]. However, there is still a challenge in developing a simple spinning method that can produce high strength CNT yarns continuously with industrial scale up.

In recent years, the dry method that directly spun CNT yarns from SACNT arrays attracted much attention because it was simple and controllable to produce CNT yarns continuously [15–23]. The spinning process converted the vertical alignment of CNTs in a SACNT array into the horizontal alignment of CNTs in a spun yarn. The freshly spun yarn consisted of loose CNTs and thus had a low strength. To obtain a strong yarn, two methods were developed, i.e. solvent shrinking and twisting. Our group used volatile solvents to shrink a freshly spun yarn [16]. The shrunk yarn had a high tensile strength of about 0.6 GPa, but possessed an irregular shaped cross section which was unfavorable for applications and the study of the shrinking mechanism. Baughman's group used a twisting method to make single- or multi-ply twisting CNT yarns with a regular round shaped cross section, but the yarns have relatively low tensile strengths in the range of 0.2–0.5 GPa [19]. Thereafter, some efforts were made to enhance the strength of the twisted yarns. Zhu's group used a two-step twisting method involving a spin twisting process and a post-spin twisting process, which improved the tensile strength of the CNT yarns up to more than 1 GPa [21]. However,

this method is inconvenient for continuous production of long CNT yarns. Tran *et al* used a modified twisting method by adding a tensioning zone in the twisting system, and obtained CNT yarns with tensile strengths up to 1 GPa [23]. However, the tensioning zone introduced an extra tension force, which was unfavorable for preparing ultra-thin yarns that could easily break due to the tension force during the twisting process.

Here we report a simple and continuous spinning method that combines the twisting and shrinking processes. In this method, a freshly spun CNT yarn is first twisted and then passes through a volatile solvent for shrinking. The produced CNT yarn forms a regular cylindrical line with a uniform diameter and consists of densely packed CNTs, and thus has a tensile strength up to about 1 GPa. The diameter of the yarn can be controlled ranging from several micrometers to tens of micrometers. The tensile strength depends on the diameter and the twisting angle of the yarn. Different kinds of solvents, such as water, ethanol, and acetone, are used to shrink CNT yarns, and the effect of solvent shrinking is investigated. This method is favorable for industrial scale continuous production of high strength CNT yarns with a wide range of diameters, especially ultra-thin CNT yarns, which can be used as high strength and ultra-thin conducting wires with a diameter less than 10 μm.

2. Experimental investigation

2.1. Spinning process of continuous CNT yarns

CNT yarns were spun from SACNT arrays (235 μm in height) synthesized on 4-inch silicon wafers [16]. The spinning setup is shown in figure 1(a). First, a wafer of SACNT array was sliced into long strips (figure 1(b)). A long strip of SACNT array was attached to and rotated together with a rotating motor, so that the CNT yarn drawn from it was twisted. Then the twisted yarn passed through a glass vessel containing a kind of solvent (water, ethanol, or acetone) and further through a small tube furnace set at 100 °C to bake out the residual solvent for shrinking. The finally obtained CNT yarn after the twisting and shrinking processes, was dry and made of pure CNTs. It was collected by a low-speed rotating motor. The CNTs in the SACNT array are multi-walled (figure 1(c)), and thus the obtained CNT yarns consist of multi-walled CNTs. In this method, the spinning process was continuous until the long strip of the SACNT array was completely consumed, producing a CNT yarn tens to hundreds of meters long (figure 1(d)). Typically, an 8 cm long strip of SACNT array can produce a CNT yarn 50–100 m long. In principle, the CNT yarns can be mass produced by replacing the SACNT array piece by piece, which was favorable for industrial scale up.

2.2. Preparation of yarns with various diameters and twisting angles

It was essential to keep the width of the SACNT array constant during the drawing process to obtain a yarn with a uniform diameter. To achieve this goal, we scanned a CO_2 laser beam on the surface of the SACNT array to etch two parallel lines at a desired distance (figure 1(b)). The laser power was 6 W with

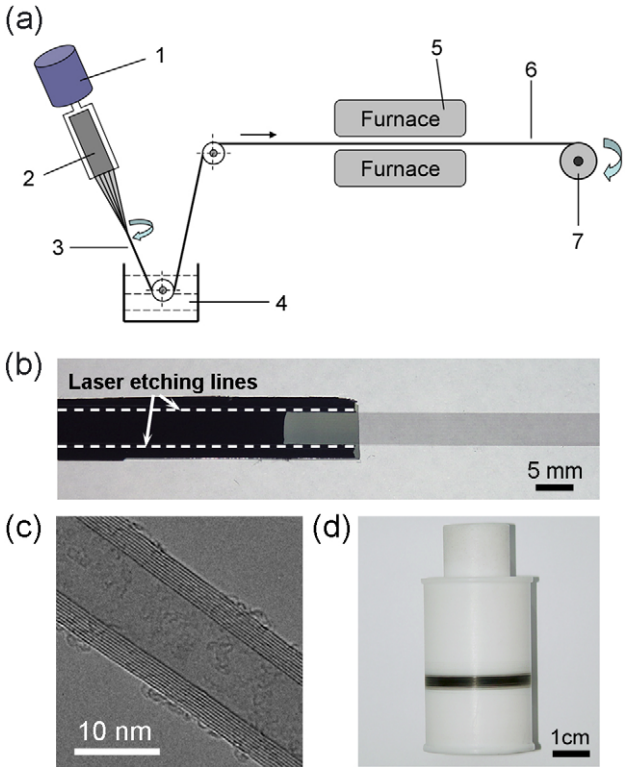

Figure 1. Spinning setup and CNT yarns. (a) An illustration of the spinning setup: (1) a rotating motor for twisting; (2) a long strip of SACNT array; (3) a twisted yarn; (4) immersing the yarn in a glass vessel containing solvent; (5) a tube furnace for baking; (6) the final CNT yarn after shrinking; (7) a rotating motor for yarn collection. (b) A long strip of SACNT array after laser etching. The effective SACNT array for producing yarns is restricted between the two etching lines and is about 5 mm in width in this figure. (c) Transmission electron microscopy (TEM) image of CNT in SACNT arrays. (d) 40 m long CNT yarn collected on a winder. The diameter of the yarn is about 10 μm.

a 10.6 μm wavelength, and the scanning rate was 10 mm s^{-1}. CNTs at the two parallel etching lines were destroyed after the laser scanning and thus could not be drawn out, which assured a uniform diameter of the resulting CNT yarn.

A twisting angle formed between the axis of the yarn and the direction of the alignment of CNTs after the yarn was twisted. It indicated the extent of the twisting effect. To prepare yarns with various twisting angles, we fixed the rotating speed of the twisting motor at about 1700 rpm (rotations per minute), and varied the rotating speed of the collecting motor in the range of 1.5–10 rpm. The diameter of the roller on the collecting motor is 28.6 mm.

2.3. Measurement of the properties of yarns

The diameters and the twisting angles of the yarns were measured under a scanning electron microscope (SEM, FEI Tecnai 100). The mechanical properties were measured by an INSTRON 5848 MicroTester at a gauge length of 20 mm and stretch rate of 0.4 mm min^{-1}. The electrical resistance was measured by a four-probe method using a KEITHLEY 2001

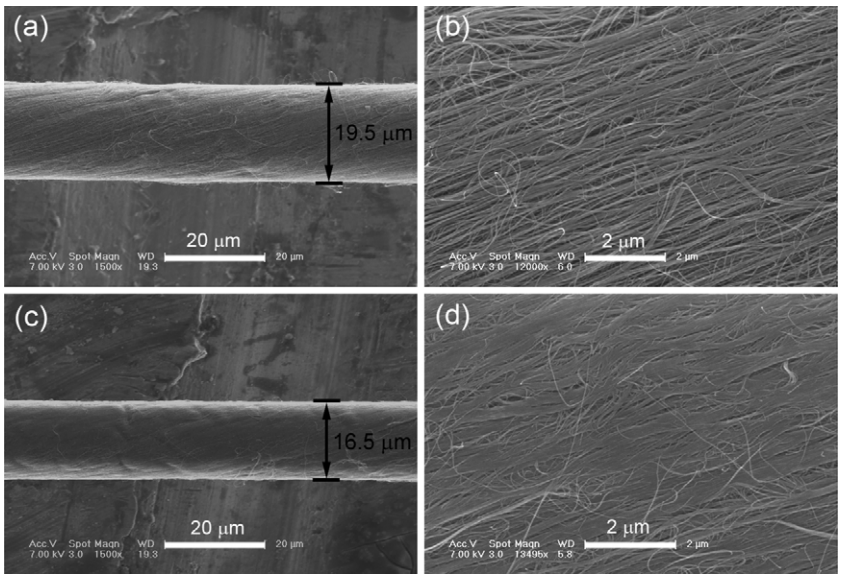

Figure 2. Twisted yarns before and after acetone shrinking. ((a), (b)) SEM images of a twisted yarn before shrinking. ((c), (d)) SEM images of a twisted yarn after shrinking.

Multimeter. At least five samples were measured under the same conditions in this work.

3. Results and discussions

3.1. Morphology of the twisted yarns before and after shrinking

Twisting is a method to densify a CNT yarn by reducing the interspaces between CNTs [23]. After twisting, a CNT yarn forms a regular cylindrical line with a uniform diameter (figure 2(a)). After further passing though a solvent, e.g. acetone, the twisted CNT yarn retains its cylindrical shape, but its diameter is evidently reduced (figure 2(c) versus (a)), which suggests that the yarn is shrunk by acetone. SEM images show that CNTs in this twisted yarn after shrinking are packed more densely than those in the twisted yarn before shrinking (figure 2(d) versus (b)). This indicates that the solvent shrinking effect further reduces the interspaces among CNTs in the yarn and densifies the yarn.

3.2. Properties of the CNT yarns after twisting and shrinking

By the laser etching method, the width of the SACNT array is controlled at 0.6–30 mm in this work, and the yarn diameter ranges from 5 to 41 μm before shrinking and from 4 to 34 μm after shrinking. The yarn diameter can be made larger or smaller by extending the range of the controlled width of the SACNT array. Figure 3(a) shows the dependence of the tensile strengths on diameter for the twisted yarns before and after shrinking. It is evident that the twisted yarns after shrinking have higher tensile strengths than those before shrinking. The CNT yarns with diameters at around 10 nm show the highest tensile strengths which are about 1.10 GPa for a twisted yarn after shrinking and 0.63 GPa for a twisted yarn before shrinking. The tensile strength reduces with increasing yarn diameter when the diameter is above 10 μm, which is due to more defects in a yarn with a larger diameter. As is known, CNT yarns drawn from an SACNT array consist of end-to-end joined CNTs [16, 18]. In a yarn with a larger diameter, there are more joined CNT ends which are weakly connected, and thus the yarn is easily broken out when being drawn. As a result, a yarn with a smaller diameter has a larger tensile strength. However, as shown in figure 3(a), when the yarn diameter is below 10 μm, the tensile strength also decreases. The reason may lie on the slight damage to the yarn surface during the handling process of yarns for mechanical measurements, which has a vital influence on the tensile strength of an ultra-thin yarn with a diameter below 10 μm but is negligible for a thick yarn with a diameter above 10 μm. Figure 3(b) shows the stress–strain curves of a twisted yarn before and after shrinking. After shrinking, the maximum strain of the yarn remains unchanged ($\sim$2.3%, in figure 3(b)), but the Young's modulus ($\sim$56 GPa) is slightly increased compared with that before shrinking ($\sim$48 GPa).

Besides their excellent mechanical properties, CNT yarns are electrically conductive. As shown in figure 3(c), the electrical resistivity decreases with reducing yarn diameter. At diameters below 20 μm, the resistivity remains almost constant at 1.1×10^{-5} Ω m. For comparison, we also measured the electrical and mechanical properties of a typically thin metal wire, i.e. a gold wire with a diameter of 18 μm. The resistivity of the CNT yarns after twisting and shrinking is two–three orders of magnitude higher than that of the gold wire ($\sim 2.5 \times 10^{-8}$ Ω m by a four-probe method), indicating that CNT yarns have no superiority to metal wires in electrical conductivity. However, the CNT yarns (tensile strength 0.6–1.1 GPa, specific strength 1.56–1.71 GPa $(\mathrm{g\ cm^{-3}})^{-1}$) are much stronger and lighter than thin gold wire (tensile strength $\sim$155 MPa, specific strength $\sim$8 MPa $(\mathrm{g\ cm^{-3}})^{-1}$), and superior to metal wires as ultra-thin conductive wires with a diameter less than 10 μm (figure 3(d)), because metal wires can rarely be produced with

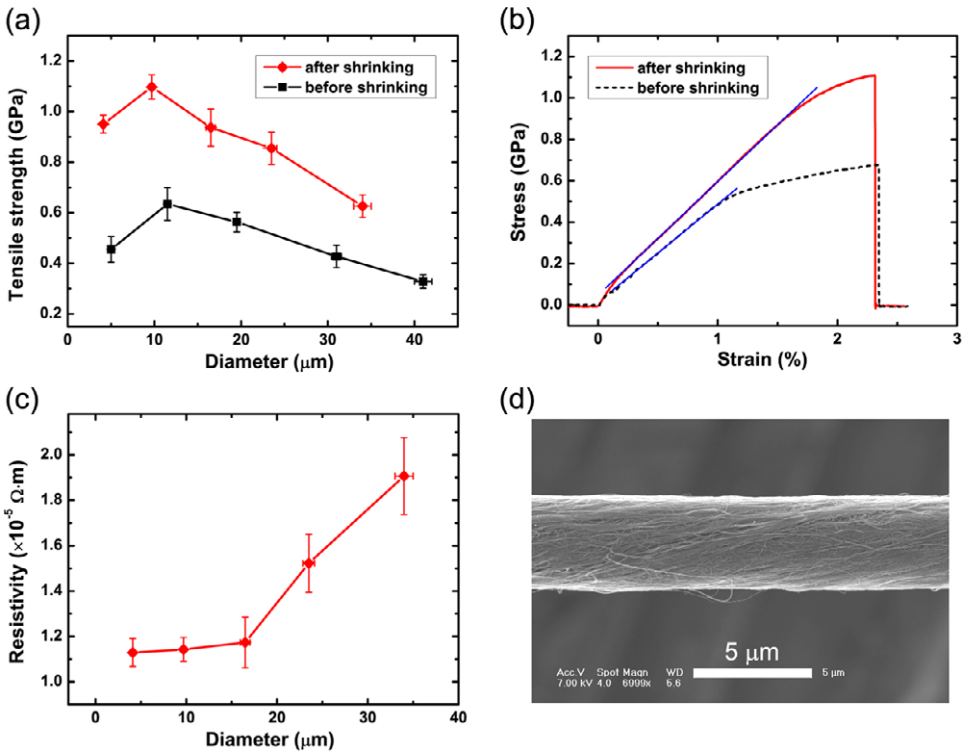

Figure 3. Mechanical and electrical properties of CNT yarns. (a) Tensile strengths of the twisted yarns before and after acetone shrinking. (b) Stress–strain curves of a twisted yarn before and after acetone shrinking. The diameter of the yarn is 11.5 μm before shrinking and 9.7 μm after shrinking. The straight lines indicate the tangent lines for calculating the Young's moduli. (c) Resistivity of the CNT yarns after twisting and shrinking. (d) An ultra-thin CNT yarn after twisting and shrinking with a diameter of 4 μm. The twisting angles of the CNT yarns after twisting and shrinking are all controlled at 12°–15°.

a diameter less than 10 μm in industry. These advantages may open up some new applications of CNT yarns as strong conductive wires, e.g. as planted wires in human bodies.

For a twisted yarn, the twisting angle indicates the extent of the twisting effect. A larger ratio of the rotating speed of the twisting motor to that of the collecting motor will create a larger twisting angle. We found that when the twisting angle was lower than 10°, the produced yarn was flattened rather than round in cross section, while when increasing the drawing angle to more than 10°, the yarn became a regular cylindrical line. Figure 4 shows the dependence of the mechanical properties of CNT yarns on twisting angles in the range of 10°–40°. With increasing twisting angle, the tensile strength and the Young's modulus both monotonously reduce (figure 4(a)), while the maximum strain at fracture increases (figure 4(b)). This indicates that a CNT yarn twisted to a larger extent possesses a larger stretchability but lower strength and modulus.

3.3. The shrinking effect on diameter and maximum load of yarns

To study the effect of the solvent shrinking, we compared the change of the diameter and the maximum load of a yarn before and after shrinking. As shown in figure 5(a), after acetone shrinking, the diameter of a yarn evidently decreases, while the maximum load that the yarn can bear increases. The percentage of the diameter reduction ranges from 15% to 24%, and the percentage of the load enhancement ranges from 15% to 40% (figure 5(b)).

The diameter reduction after shrinking indicates that a CNT yarn is densified with a reduction of the interspaces among CNTs due to the shrinking effect of acetone, and as a result, the van der Waals forces among CNTs are increased. This will give rise to strong friction forces among CNTs along the yarn axis when the yarn was stretched, inducing an enhancement of the yarn strength. Therefore the maximum load that the yarn can bear is enhanced.

Similar to solvent shrinking, twisting also has the effect of densification of the yarns [19, 23]. However, as implied by the fact that the solvent shrinking can further reduce the yarn diameter, mechanical twisting does not fully densify the CNT yarns. This is why the merely twisted CNT yarns have relatively low tensile strengths, which are 300–600 MPa in this work and 300–500 MPa reported by Baughman's group [19]. Therefore to enhance the strength of a yarn, a further densification is required. Tran *et al* used a mechanical method by adding a tensioning zone to introduce an extra tension force along the yarn axis in the twisting process, which improved the alignment of CNTs in a yarn and densified the yarn [23]. However, the extra tension force may be fatal for the fabrication of ultra-thin yarns, which may easily break when applying a tensile force in the twisting process. In contrast, we used a solvent treatment of CNT yarns for further densification which did not introduce any extra tensile forces along the yarn axis in the twisting process. Therefore, our method can be

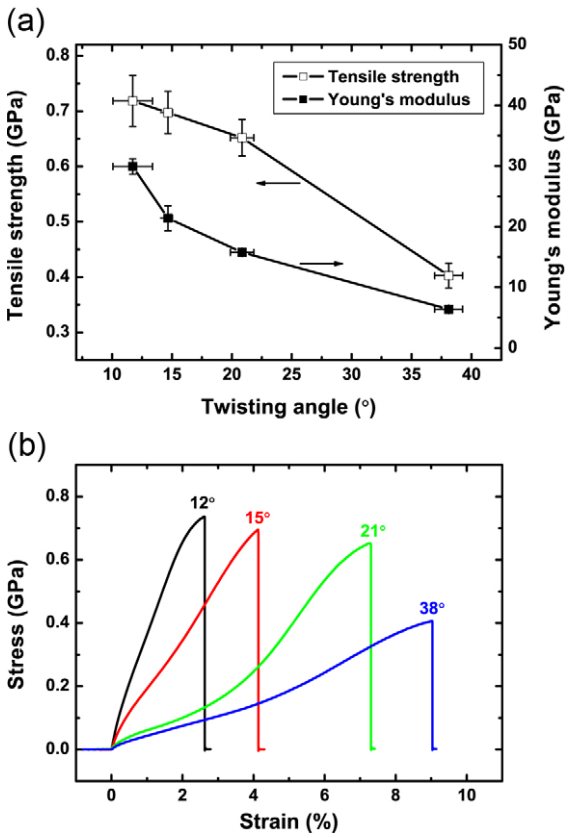

Figure 4. The dependence of the mechanical properties of the CNT yarns on twisting angles after twisting and shrinking. (a) Tensile strengths and Young's moduli at different twisting angles. (b) Stress–strain curves at different twisting angles. All the yarns were spun from a 2 cm wide SACNT array, and their diameters were about 25 μm after shrinking.

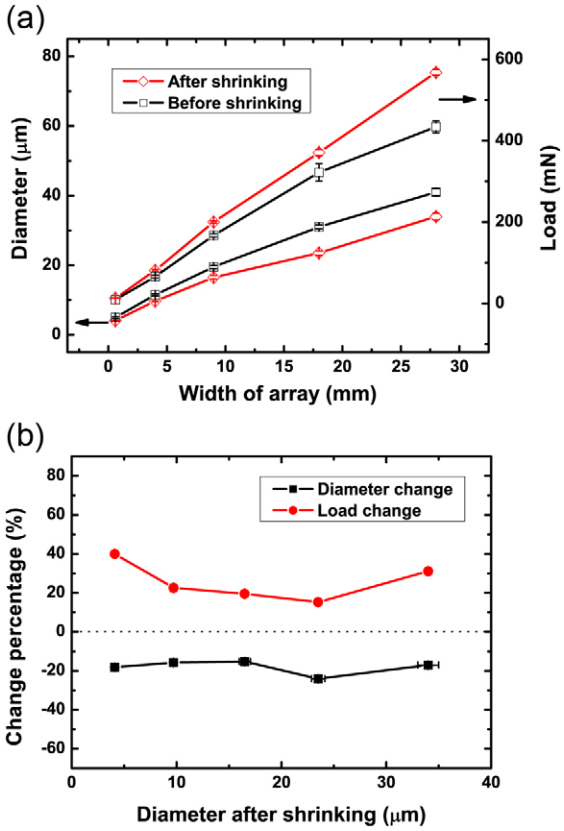

Figure 5. Shrinking effect of acetone on the twisted yarns. (a) Diameters and maximum loads of the twisted yarns before and after shrinking. The x axis is the width of the SACNT array where a yarn was drawn out. (b) Change percentage of diameters and maximum loads of the yarns after and before shrinking.

used for fabricating CNT yarns with a wide diameter range, especially for fabricating ultra-thin yarns.

3.4. Discussion on the origin of the solvent shrinking effect

As is known, CNTs drawn out from SACNT arrays are hydrophobic but can be wetted by most of the common organic solvents [16, 20]. The surface tension is considered to play a vital role on the shrinking effect of organic solvents for the untwisted yarns, and a possible reason is that the meniscus pinched the yarn tightly when the yarn was pulled out from the organic solvent [16].

Here, to explore the shrinking effect in depth, we applied three common solvents, i.e. water, ethanol, and acetone, to shrink yarns in our spinning system. Water has a very strong surface tension (72.14 mN m^{-1} at 25 °C [24]) compared with most of the common organic solvents, such as ethanol (21.97 mN m^{-1} at 25 °C [24]) and acetone (23.46 mN m^{-1} at 25 °C [24]), but does not wet with CNTs. After the yarn passed through water, the diameter of the yarn was reduced while the maximum load was slightly increased (figures 6(a) and (b)), inducing an enhancement of the tensile strength (figure 6(c)), which suggested that the yarn was shrunk by water. However, because of the hydrophobic property of CNTs, water could hardly infiltrate inside the yarn during the short time when the yarn passed through water. Thus the yarn should be compressed merely through its surface by the surface tension of water. As shown in figure 6(d), the yarn after water shrinking has a rough surface compared with the yarns after organic solvent shrinking with a smooth surface (figure 2(c)), showing a trace of the surface-compressed process.

In contrast with water, the organic solvents, ethanol and acetone, both wet with CNTs. Therefore they could easily infiltrate into a yarn and fill the interspaces among CNTs as the yarn passes through them. For a twisted yarn, the shrinking process may occur firstly at the interface where the yarn was pulled out from the organic solvent as aforementioned [16]. But according to our observation, the diameter of the yarn was further reduced after the yarn was dried by the tube furnace. It suggested that a further shrinking process occurred when the organic solvent infiltrating into the yarn was vaporized, which was possibly realized by drawing CNTs closer due to the surface tension of the organic solvent. Therefore, the mechanism of organic solvent shrinking differs from that of water shrinking, but they both result from the surface tension of the solvents. Furthermore, although acetone and ethanol have similar surface tension, acetone diffuses much more quickly in CNT films or yarns than ethanol as we observed, and thus has a better wettability with CNTs. This will induce more sufficient infiltration of acetone into the yarn during the short time when the yarn passes through acetone, and as a result, acetone has a

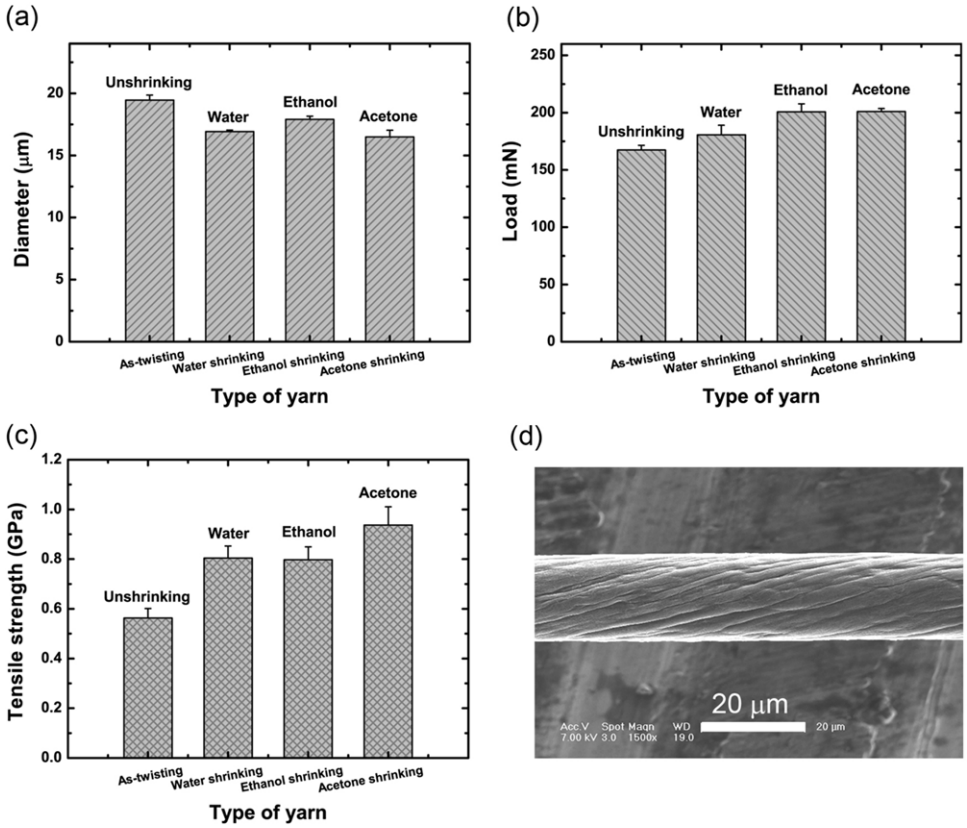

Figure 6. Twisted yarns before and after shrinking using different solvents. (a) Comparison of yarn diameters. (b) Comparison of maximum loads. (c) Comparison of tensile strengths. (d) SEM image of a yarn after water shrinking. All the yarns were drawn out from a 1.8 cm wide SACNT array.

better shrinking effect than ethanol, as shown in figures 6(a)–(c). That is why acetone was used to shrink the twisted yarns to achieve high tensile strengths in this work.

4. Summary

To summarize, we combine the twisting and shrinking processes to produce carbon nanotube yarns from super-aligned carbon nanotube arrays in this work. The as-produced CNT yarns consist of densely packed CNTs, and thus have tensile strengths up to about 1 GPa. The diameters of the yarns can be controlled ranging from several micrometers to tens of micrometers. The tensile strength shows a peak value at a yarn diameter of about 10 μm, and decreases with increasing twisting angle. Three common solvents, water, ethanol, and acetone, have been used to shrink CNT yarns, and acetone shows the best shrinking effect. The mechanism of the ethanol and acetone shrinking differs from that of the water shrinking, but they both result from the surface tension of the solvents. Our method is favorable for continuous mass production of high strength yarns with a wide range of diameters, especially ultra-thin yarns.

Acknowledgments

This work was financially supported by the National Basic Research Program of China (2005CB623606, 2007CB935301), NSFC (10704044, 50825201, 10721404), Fok Ying Tung Education Foundation (111049), and a China Postdoctoral Science Foundation funded project (20080440025, 200902078). We thank Professor Yadong Li for his helpful discussion.

References

[1] Yu M F, Lourie O, Dyer M J, Moloni K, Kelly T F and Ruoff R S 2000 *Science* **287** 637–40
[2] Yu M F, Files B S, Arepalli S and Ruoff R S 2000 *Phys. Rev. Lett.* **84** 5552–5
[3] Peng B, Locascio M, Zapol P, Li S Y, Mielke S L, Schatz G C and Espinosa H D 2008 *Nat. Nanotechnol.* **3** 626–31
[4] Vigolo B, Pénicaud A, Coulon C, Sauder C, Pailler R, Journet C, Bernier P and Poulin P 2000 *Science* **290** 1331–4
[5] Dalton A B, Collins S, Muñoz E, Razal J M, Ebron V H, Ferraris J P, Coleman J N, Kim B G and Baughman R H 2003 *Science* **423** 703
[6] Ericson L M *et al* 2004 *Nature* **305** 1447–50
[7] Miaudet P, Badaire S, Maugey M, Derré A, Pichot V, Launois P, Poulin P and Zakri C 2005 *Nano Lett.* **5** 2212–5
[8] Kozlov M E, Capps R C, Sampson W M, Ebron V H, Ferraris J P and Baughman R H 2005 *Adv. Mater.* **17** 614–7
[9] Cheng H M, Li F, Su G, Pan H Y, He L L, Sun X and Dresselhaus M S 1998 *Appl. Phys. Lett.* **72** 3282–4
[10] Zhu H W, Xu C L, Wu D H, Wei B Q, Vajtai R and Ajayan P M 2002 *Science* **296** 884–6
[11] Li Y L, Kinloch I A and Windle A H 2004 *Science* **304** 276–8

[12] Koziol K, Vilatela J, Moisala A, Motta M, Cunniff P, Sennet M and Windle A 2007 *Science* **318** 1892–5
[13] Ma W J *et al* 2009 *Adv. Mater.* **21** 603–8
[14] Ma W J *et al* 2009 *Nano Lett.* **9** 2855–61
[15] Jiang K L, Li Q Q and Fan S S 2002 *Nature* **419** 801
[16] Zhang X B, Jiang K L, Feng C, Liu P, Zhang L N, Kong J, Zhang T H, Li Q Q and Fan S S 2006 *Adv. Mater.* **18** 1505–10
[17] Liu K, Sun Y H, Chen L, Feng C, Feng X F, Jiang K L, Zhao Y G and Fan S S 2008 *Nano Lett.* **8** 700–5
[18] Liu K, Sun Y H, Liu P, Wang J P, Li Q Q, Fan S S and Jiang K L 2009 *Nanotechnology* **20** 335705
[19] Zhang M, Atkinson K R and Baughman R H 2004 *Science* **306** 1358–61
[20] Zhang M, Fang S L, Zakhidov A A, Lee S B, Aliev A E, Williams C D, Atkinson K R and Baughman R H 2005 *Science* **309** 1215–9
[21] Zhang X F, Li Q W, Tu Y, Li Y, Coulter J Y, Zheng L X, Zhao Y H, Jia Q X, Peterson D E and Zhu Y T 2007 *Small* **3** 244–8
[22] Zhang X F *et al* 2007 *Adv. Mater.* **19** 4198–201
[23] Tran C D, Humphries W, Smith S M, Huynh C and Lucas S 2009 *Carbon* **47** 2662–70
[24] Dean J A 1999 *Lange's Handbook of Chemistry* (New York: McGraw-Hill)