Polymers & biopolymers



Dyeable electroconductive cotton wrapped CNT yarn for multifunctional textiles

Ke Jia¹, Wei Chen², Jianing Wang¹, Fujun Xu², and Wei Liu^{1,*} (D)

¹ School of Textiles and Fashion, Shanghai University of Engineering Science, Shanghai 201620, People's Republic of China ² Key Laboratory of Textile Science and Technology, Ministry of Education, College of Textiles, Donghua University, Shanghai 201620, People's Republic of China

Received: 3 September 2021 Accepted: 27 September 2021 Published online: 3 January 2022

© The Author(s), under exclusive licence to Springer Science+Business Media, LLC, part of Springer Nature 2021

ABSTRACT

Conductive fiber plays increasingly important role in the field of multifunctional textile and smart clothing for the signal/power transmission, electrothermal function and so on. However, their major bottle necks are rigid, undyeable and limited durability. In this study, we manufactured a dyeable, washable and flexible conductive yarn by wrapping cotton roving fiber (wrapped fiber) on the surface of Carbon Nanotube (CNT) fiber (core yarn) and twisting them together by core-spun yarn spinning technique, named as cotton wrapped CNT yarn (CWC yarn). The appearance and flexibility of the CWC yarn are similar with the cotton yarn, but showing excellent conductivities of 100 Ω /cm, (undyed CWC yarn) and 50 Ω /cm (dyed CWC yarn). The electrothermal temperature of the CWC yarn with length of 5 cm reached 70 °C with applied voltage of 20 V, which was even higher than that of the pristine CNT yarn (60 °C). Furthermore, its electrical and electrothermal property changed slightly after being loaded, bent, knotted, fold-released (100 cycles) and washed, showing excellent durability. In addition, the electrochromatically dyed CWC yarn after weaving or embroidering into fabrics displayed changed colors with the various applied voltages. This work demonstrated a simple and referential method to design dyeable and washable multifunctional yarns for wearable applications.

Introduction

Wearable devices of intelligent textiles have been widely concerned and studied for their friendly interface with human body as well as various functions they provide. These devices are widely used as strain sensors [1–3], electronic skins [4], health monitoring systems [5, 6], super capacitors [7, 8] and so forth. As an important part of the wearable device, conductive fiber is critical to connect the functional elements together to supply the

Handling Editor: Stephen Eichhorn.

Address correspondence to E-mail: wliu@sues.edu.cn

electrical power or transmit signal. Among the conductive fibers, carbon-based conductive fibers are being considered as promising candidates for their remarkable mechanical, electrical, thermal and optical properties [9, 10]. Some scholars dispersed CNT or graphene on the surface of yarns or fabrics by impregnation method to obtain flexible conductive textiles [11–13]. However, the self-entanglement and aggregation hinder the uniform dispersion of the CNTs in the aqueous solution, resulting in limited conductivity [14]. Moreover, the exposure of the CNTs to the surface of the substrate textiles causes the poor dyeability, durability and washability.

In recent decades, the aerogel-spun CNT yarn fabricated by floating catalyst chemical vapor deposition (FCCVD) shows a variety of advantages of high tensile strength, extraordinary structural flexibility, high electrical conductivity and outstanding corrosion/oxidation resistivity [15, 16], which makes it ideal for wearable electronics. For examples, Ma et al. [17] produced core/sheath structured highly sensitive strain varn sensor by partially compositing CNT yarn with epoxy/acetone polymer solution to detect the tiny deformation of human skin. Wu et al. [9] manufactured a super elastic and electroconductive fiber by wrapping a flexible and conductive carbon nanotube/polydimethylsiloxane composite yarn onto a polyester filament for stretchable wearable electronics. Furthermore, over-twisted CNT fibers showed excellent stretching fatigue property and stable conductivity, that can be applied as stretchable conductor, actuator, even artificial muscle [18, 19]. After the CNT fibers/yarns were physically modified by annealing [20], cyclic stretching [21, 22], capillary force induced condensing [23] or chemically modified by acid treatment [24], plasma treatment [25], doping methods [26], its mechanical and electrical properties can be further enhanced. However, the intrinsically black color and undyeable inert surface limits the aesthetics design and practical applications.

In this study, a conductive yarn, named cotton wrapped CNT yarn (CWC yarn), was made by wrapping the cotton fiber on the surface of CNT yarn and twisting together. Its electrical, mechanical and thermal properties were characterized. In addition, the weaving property, dyeing property and electrochromic property of the CWC yarn were investigated. The CWC yarn embedded multifunctional fabric was also demonstrated as well.

Materials

Pristine CNT yarns, as shown in Fig. 1a and b, with diameter around 50 µm were provided by Suzhou Jiedi Nano Technology Co., Ltd. The CNT yarn was spun directly from the chemical vapor deposition (CVD) synthesis zone of a furnace using a liquid source of carbon and an iron nano-catalyst [27, 28]. Other materials include pure cotton roving (3 Nm, Changzhou yanghu shuntian textile Co., Ltd), dyestuff (Red, yellow, green; Jinan yuanbaolai Chemical Technology Co., Ltd), Polyurethane (Dongguan BOGAO Chemical Co., Ltd), thermochromic inks (40 °C for the conversion temperature, colorless to green, Shenzhen Oriental Color Technology Co., Ltd) and conductive silver paste (Kunshan Chuang Wei Lvyuan Electronics Co., Ltd) were purchased from the commercial market.

Characterizations

The optical picture of the surface morphology was tested by SLR camera (SONY ILCA-77M2). The optical microscope and SEM image of the cross section were tested by optical microscope (GP-300C, Kunshan Gaopin Precision Instrument Co., Ltd) and scanning electron microscope (JEOL JSM-6490 LV). The tensile properties were tested by tensile instrument (XS(08)XT-3, Shanghai xusai Instrument Co., Ltd).

The resistance was tested by the resistance tester (keysight 34450A, Agilent Technologies Co., Ltd). The E-heating performance was tested by the infrared thermal image devices (S/N225, Shanghai Reimage Technology Co., Ltd), which powered by the DC power source (DP831A, Beijing Puyuan Jingdian Technology Co., Ltd).

Results and discussion

Fabrication and structure

Figure 2a showed the schematic of CWC yarn preparation process. Pure cotton roving was introduced into the compact spinning system at first. As following, the CNT yarn was introduced into the wrapping and twisting zone between the front roller **Figure 1** a Optical picture and b SEM image of the CNT yarn.



and compressed apron. In this way, the CNT yarn was tightly wrapped by the cotton fibers and thus CWC yarn was obtained. As shown in Fig. 2b and c, the optical figure and its amplified picture showed the cotton fibers on the outer surface of CWC yarn formed a uniform spiral wrapped structure. The CWC yarn showed an average diameter of about 0.7 mm, which was suitable for weaving processing and wearable applications. Its cross-sectional view as shown in Fig. 2d and e showed that the inner CNT yarn with a diameter of $\sim 50 \,\mu\text{m}$ was tightly surrounded by cotton fibers. Therefore, cotton yarn-like appearance provides CWC yarn great potentials to the wearable applications.

Electrical and electrothermal performance

Figure 3 showed the electrical and electrothermal performance of CNT yarn and CWC yarn with length of 5 cm. As shown in Fig. 3a, the E-heating

temperatures of both yarns remarkably increased with the applied voltages rising from 5 V to 22.5 V. As applied by the same voltage, the CWC yarn showed higher E-heating temperatures than the CNT yarn. The highest E-heating temperature of the CWC yarn reached 81.3 °C at 22.5 V, which is around 10 °C higher than that of the CNT yarn. This is because the wrapped cotton fiber provided a thermal insulation layer on the CNT yarn, which hindered the heat dissipation and enhanced surface temperature. The infrared images as shown in Fig. 3b exhibited the uniform temperature distribution. The temperatures of the CWC yarn raised immediately in a few seconds and then reached maximum values as shown in Fig. 3c, showing a quick response to the applied voltages. When the power supply was cut off, the CWC yarn cooled down rapidly to the ambient temperature.

Figure 3d showed the real-time changing temperature of CWC yarn as the applied voltage switching



🙆 Springer



Figure 3 a Electrothermal temperature as a function of applied voltage. b Infrared images of 5 cm-long CNT and CWC yarn with various applied voltage. c Electrothermal temperature curves of CWC yarn as a function of time. d Electrothermal temperature

curve of CWC yarn with the switched voltage from 5 to 15 V. e Electrical resistance of CNT and CWC yarn with various lengths and f after five times washing.

from 5 to 15 V for 100 cycles. The temperatures of the yarn were stable at 5 V (~ 29 °C) and 15 V (~ 46 °C), indicating its repeatable and reliable electrothermal property. As shown in Fig. 3e, the electrical resistances of both CNT yarn and CWC yarn increased linearly from ~ 100 Ω to ~ 480 Ω with yarn length increased from 1 to 5 cm, which indicates the core CNT yarn in the wrapped yarn is straight and intact. To investigate the reliability of the CWC yarn, the yarn was washed for imitating the real wearable application. It was hand washed in a soap water solution with 4 g/L concentration at 40 °C for 5 min and dried at room temperature. As shown in Fig. 3f, after five repeated washing cycles, the resistance of the CWC yarn was slightly changed.

Mechanical properties

Figure 4a showed the load strain curve of both CNT and CWC yarn. Due to its limited diameter ($\sim 50 \ \mu m$), the pure CNT yarn can only bear 0.25 N load. While the CWC yarn showed higher tensile breakage load ($\sim 7 \ N$) due to the support of the wrapped cotton fibers. As shown in Fig. 4b, after 100

cycles of bending and releasing, the electrical resistance of the yarn was slightly changed. Furthermore, the uniform infrared images of the CWC yarn with bending and knotting was shown in Fig. 4c and d, indicating its excellent flexibility. Figure 4e showed that the CWC yarn possessed stable conductivity and kept a LED light lighting even under 200 g loading.

Electrothermal performance of the CWC yarn embedded fabric

The CWC yarn can be woven into a fabric. Figure 5a showed the CWC yarn was interlaced into a cotton fabric as weft yarn. Due to the cotton surface appearance and flexibility of the yarn, the fabric looks as same as a normal woven cotton fabric. With folding the fabric into different angles from 135° to 0° as shown in Fig. 5b, the variation of its resistance was lower than 8Ω ($353 \sim 361 \Omega$). Due to the cotton fiber provides protecting outer layer for the CNT core yarn, the CWC yarn obtained good durability. Even after 100 folding–releasing cycles, the resistance still maintained around 360Ω as shown in Fig. 5c. In addition, a single CWC yarn was embroidered into a



Figure 4 a Comparison of tensile properties of the CWC yarn, CNT yarn and cotton yarn. b Resistance changing ratios of the CWC yarn under 100 bending cycles. Optical and infrared images

of the CWC yarn after multiple c bending and d knotting. e Demonstration of the conductive behavior of the CWC yarn under 200 g loading.



Figure 5 a Schematic diagram and physical diagram of the woven cotton fabric interlaced by CWC yarn. b CWC yarn embedded fabric folding into different angles. c Resistance of the CWC yarn

cotton fabric with a pattern of "SUES". By connecting the two ends of the yarn to an electric power, the pattern can be E-heated with clear "SUES" letters showed in its infrared image in Fig. 5e.

Color changing performance of the CWC yarn embedded fabric

The CWC yarn has good dyeability that it can be dyed into different colors. As shown in Fig. 6, the CWC yarns were dyed into red, white, green and yellow colors by using the commercial dyes (Reactive dye) and then used as conductive wires to light LEDs. The dyed CWC yarn was also flexible and can be embroidered into cotton fabrics in Fig. 6b. in fabric with cyclic folding. **d** Optical picture and infrared images of the CWC yarn stitched pattern in cotton fabric.

Unexpectedly, as shown in Fig. 6c, the conductivity of dyed CWC yarn increased due to the core CNT yarn can be densified by ethanol in dye solution [29]. Additionally, after coating by the electrochromatic ink, the CWC yarn in its embedded fabric displayed obvious color changing from white to green with applied voltages increased from 5 to 15 V as shown in Fig. 6d. This is due to the temperature of CWC yarn enhanced from 28.5 to 57.9 °C as the voltage increased.





Figure 6 a Demonstration of the dyed CWC yarn as conductive wires. b Wearable electrical circuit with dyed CWC yarn. c Resistance of the dyed CWC yarn. d Optical and infrared images of the eletro-thermochromatic coated fabric under different voltages.

Conclusion

In this study, the CWC yarn was prepared by wrapping the cotton fiber on the CNT yarn via corespun yarn spinning technique. The experimental results showed that the similar appearance, flexibility, washability, durability and dyeability with common cotton yarn, but excellent conductivity and electrothermal property over it. The CWC yarn showed good conductivity and electrothermal property after bending, loading, knotting, cyclic foldingreleasing and repeated washing. Moreover, the CWC yarn can be easily dyed by commercial dye. After being woven or embroidered into cotton fabric, the dyed CWC yarn still exhibited excellent electrical and electrothermal property.

Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

- Wang W, Yu A, Zhai J, Wang ZL (2021) Recent progress of functional fiber and textile triboelectric nanogenerators: towards electricity power generation and intelligent sensing. Adv Fiber Mater. https://doi.org/10.1007/s42765-021-0007 7-9
- [2] Cai G, Yang M, Pan J, Cheng D, Xia Z, Xin W, Tang B (2018) Large-scale production of highly stretchable CNT/ Cotton/Spandex composite yarn for wearable applications. ACS Appl Mater Interfaces 10(38):32726–32735. https://d oi.org/10.1021/acsami.8b11885
- [3] Liu W, Liu N, Gao Y, Wang S, Cheng Q, Xu F (2018) Strain sensing fabric integrated with carbon nanotube yarn for wearable applications. Text Res J 89(15):3048–3055. http s://doi.org/10.1177/0040517518807441
- [4] Nela L, Tang J, Cao Q, Tulevski GS, Han SJ (2018) Large-Area high-performance flexible pressure sensor with carbon nanotube active matrix for electronic skin. Nano Lett 18(3):2054–2059. https://doi.org/10.1021/acs.nanolett.8b 00063
- [5] Lv S, Shuai L, Ding W, Ke W, Wang B, Wan J (2021) Flexible humidity sensitive fiber with swellable metal-organic frameworks. Adv Fiber Mater 3(2):107–116. https://d oi.org/10.1007/s42765-021-00064-0
- [6] Xu F, Aouraghe MA, Xie X, Zheng L, Fu KK (2021) Highly stretchable, fast thermal response carbon nanotube

composite heater. Compos Part A: Appl Sci Manuf 147(19):106471. https://doi.org/10.1016/j.compositesa.2021. 106471

- [7] Xue L, Fan W, Yu Y, Dong K, Liu C, Sun Y, Zhang C, Chen W, Lei R, Rong K, Wang Q (2021) A novel strategy to fabricate core-sheath structure piezoelectric yarns for wear-able energy harvesters. Adv Fiber Mater 3:239–250. https://d oi.org/10.1007/s42765-021-00081-z
- [8] Meng J, Nie W, Zhang K, Xu F, Ding X, Wang S, Qiu Y (2018) Enhancing electrochemical performance of graphene fiber-based supercapacitors by plasma treatment. ACS Appl Mater Interfaces 10(16):13652–13659. https://doi.org/10.10 21/acsami.8b04438
- [9] Wu J, Wang Z, Liu W, Wang L, Xu F (2019) Bioinspired superelastic electroconductive fiber for wearable electronics. ACS Appl Mater Interfaces 11(47):44735–44741. https://doi. org/10.1021/acsami.9b16051
- [10] Qin Y, Peng Q, Ding Y, Lin Z, Wang C, Li Y, Xu F, Li J, Yuan Y, He X, Li Y (2015) Lightweight, superelastic, and mechanically flexible graphene/polyimide nanocomposite foam for strain sensor application. ACS Nano 9(9):8933–8941. https://doi.org/10.1021/acsnano.5b02781
- [11] Cai G, Yang M, Pan J, Cheng D, Xia Z (2018) Large-Scale production of highly stretchable CNT/Cotton/Spandex composite yarn for wearable applications. ACS Appl Mater Interfaces 10(38):32726–32735. https://doi.org/10.1021/acsa mi.8b11885
- [12] He X, Zhang F, Wang R, Liu W (2007) Preparation of a carbon nanotube/carbon fiber multi-scale reinforcement by grafting multi-walled carbon nanotubes onto the fibers. Carbon 45(13):2559–2563. https://doi.org/10.1016/j.carbon. 2007.08.018
- [13] Yuan Y, Yin W, Yang M, Xu F, Zhao X, Li J, Peng Q, He X, Du S, Li Y (2018) Lightweight, flexible and strong coreshell non-woven fabrics covered by reduced graphene oxide for high-performance electromagnetic interference shielding. Carbon 130:59–68. https://doi.org/10.1016/j.carbon.2017.12 .122
- [14] Li X, Zhou C, Overman N, Ma XL, Canfield N, Kappagantula K, Schroth J, Grant G (2021) Copper carbon composite wire with a uniform carbon dispersion made by friction extrusion. J Manuf Process 65:397–406. https://doi. org/10.1016/j.jmapro.2021.03.055
- [15] Liu W, Xu F, Zhu N, Wang S (2016) Mechanical and electrical properties of carbon nanotube / polydimethylsiloxane composites yarn. J Eng Fiber Fabr 210(3):594–599. https://d oi.org/10.1002/pssa.201228549
- [16] Wei L, Xu F, Sun L, Wei L, Qiu Y (2016) A novel flexible humidity switch material based on multi-walled carbon nanotube/polyvinyl alcohol composite yarn. Sens Actuat B

Chem 230:528–535. https://doi.org/10.1016/j.snb.2016.02. 108

- [17] Wen YH, Tsou CH, de Guzman MR, Huang D, Yu YQ, Gao C, Zhang XM, Du J, Zheng YT, Zhu H, Wang ZH (2021) Antibacterial nanocomposite films of poly(vinyl alcohol) modified with zinc oxide-doped multiwalled carbon nanotubes as food packaging. Polym Bull. https://doi.org/10. 1007/s00289-021-03666-1
- [18] Mirzaeifar R, Qin Z, Buehler MJ (2015) Mesoscale mechanics of twisting carbon nanotube yarns. Nanoscale 7(12):5435–5445. https://doi.org/10.1039/c4nr06669c
- [19] Shang Y, He X, Li Y, Zhang L, Li Z, Ji C, Shi E, Li P, Zhu K, Peng Q, Wang C, Zhang X, Wang R, Wei J, Wang K, Zhu H, Wu D, Cao A (2012) Super-stretchable spring-like carbon nanotube ropes. Adv Mater 24(21):2896–2900. https://doi. org/10.1002/adma.201200576
- [20] Li W, Xu F, Wang Z, Wu J, Liu W, Qiu Y (2016) Effect of thermal treatments on structures and mechanical properties of aerogel-spun carbon nanotube fibers. Mater Lett 183:117–121. https://doi.org/10.1016/j.matlet.2016.07.034
- [21] Wang Z, Wu J, Wei X, Saleemi S, Liu W, Li W, Marriam I, Xu F (2019) Bioinspired microstructure-reorganized behavior of carbon nanotube yarn induced by cyclic stretching training. J Mater Chem C 8(1):117–123. https://doi.org/10. 1039/c9tc06056a
- [22] Hu G, Zhang X, Liu X, Yu J, Ding B (2020) Strategies in precursors and post treatments to strengthen carbon nanofibers. Adv Fiber Mater 2(2):46–63. https://doi.org/10.1007/ s42765-020-00035-x
- [23] Shao Y, Xu F, Liu W, Zhou M, Li W, Hui D, Qiu Y (2017) Influence of cryogenic treatment on mechanical and interfacial properties of carbon nanotube fiber/bisphenol-F epoxy composite. Compos B Eng 125:195–202. https://doi.org/10. 1016/j.compositesb.2017.05.077
- [24] Misak HE, Asmatulu R, Omalley M, Jurak E, Mall S (2014) Functionalization of carbon nanotube yarn by acid treatment. Int J Smart Nano Mater 5(1):34–43. https://doi.org/10.1080/ 19475411.2014.896426
- [25] Shao Y, Xu F, Marriam I, Liu W, Gao Z, Qiu Y (2019) Quasi-static and dynamic interfacial evaluations of plasma functionalized carbon nanotube fiber. Appl Surf Sci 465:795–801. https://doi.org/10.1016/j.apsusc.2018.09.258
- [26] Kanakaraj SN, Hsieh YY, Adusei PK, Homan B, Fang Y, Zhang G, Mishra S, Gbordzoe S, Shanov V (2019) Nitrogendoped CNT on CNT hybrid fiber as a current collector for high-performance Li-ion capacitor. Carbon 149:407–418. h ttps://doi.org/10.1016/j.carbon.2019.04.032
- [27] Aouraghe MA, Xu F, Liu X, Qiu Y (2019) Flexible, quickly responsive and highly efficient E-heating carbon nanotube



film. Compos Sci Technol 183:107824. https://doi.org/10. 1016/j.compscitech.2019.107824

- [28] Xu F, Wei B, Liu W, Zhu H, Zhang Y, Qiu Y (2015) In-plane mechanical properties of carbon nanotube films fabricated by floating catalyst chemical vapor decomposition. J Mater Sci 50(24):8166–8174. https://doi.org/10.1007/s10853-015-939 5-0
- [29] Du S, Zhao W, Yuan L (2012) Absorption and structural property of ethanol/water mixture with carbon nanotubes. Chin J Chem Phys 25(4):487–493. https://doi.org/10.1088/ 1674-0068/25/04/487-493

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.