Highly Crystalline Graphene Fibers with Superior Strength and Conductivities by Plasticization Spinning

Peng Li, Yingjun Liu, Shaoyi Shi, Zhen Xu,* Weigang Ma,* Ziqiu Wang, Senping Liu, and Chao Gao*

Graphene fiber (GF), a macroscopic one-dimensional assembly of individual graphene sheets, promises both extraordinary mechanical performance and superior multifunctionality. However, the properties of graphene fiber are still limited due to the unfavorable crystalline structures, especially induced by wrinkled conformations of graphene. A plasticization spinning strategy is presented to achieve GF with both high mechanical strength and electrical/thermal conductivity. Adjusting the interlayer space from 1.2 to 1.8 nm by intercalating proper plasticizers to adjacent graphene oxide sheets enables graphene oxide fibers to achieve a 580% enhanced deformable plasticity. Such a plasticization spinning flattens random graphene wrinkles, and regulates sheets with high order and stacking density, thereby forming large crystallite domains. The GF exhibits all around record performance including mechanical strength (3.4 GPa), electrical conductivity (1.19 × 10^6 S m^−1), and thermal conductivity (1480 W m^−1 K^−1). The optimally crystalline GF with the integration of benchmark overall properties and scalable fabrication is likely to be attractive and competitive in future industrial applications.

1. Introduction

Carbonaceous fiber is an indispensable material in aerospace, vehicles, sport products, and energy.[1–3] The long pursuit of the exclusively high mechanical performance and superior conducting functionalities in a single fiber has never stopped ever since its invention in the 1950s.[2] Graphene has been considered as theoretically fundamental elements in polyacrylonitrile (PAN), mesophase pitch (MPP) based carbon fibers (CF), and until recently, the isolation of graphene has ignited the direct assembly to create macroscopic graphene fiber (GF).[4–6] Distinct from the pyrolysis method to fuse organic fragments into tiny graphene units in PAN- and MPP-based CFs, the direct assembly of large graphene sheets promises more crystalline graphitic structures.[2] From this perspective, GF is hoped to integrate high mechanical strength with superior conducting functionalities, providing an alternative methodology to combine these two merits that are elusive in conventional CFs.

The fabrication of GF mainly relies on wet-spinning of graphene oxide (GO) liquid crystals, first created in 2011.[8] After that, GFs with high performance were continually reported to break a record, especially when high temperature graphitization was introduced to remove the defects on GO sheets and generate crystalline graphitic structures.[9–11] However, the crystalline structures of GFs are never optimized. In principle, the larger the ordered crystalline domain holds, the better the performance of fibers should be, approaching the extreme case of single-crystalline graphite whiskers.[12,13] The central mission in fabricating qualified GFs is to fashion graphene sheets into a highly crystalline order with giant and aligned crystallites. Notably, improper microstructures, like incompact stack of graphene and misaligned arrangement, still prevail in previously reported GFs, and bring poor crystallization and thus limited properties. For instance, size-mixing method allowed densification by filling voids at the expense of sheet alignment, realizing thermal conductivity (1290 W m^−1 K^−1), electrical conductivity (2.21 × 10^5 S m^−1), and tensile strength (1.08 GPa).[15] Narrowing the spinneret and wet-drafting of GO gel fibers partially improved sheet alignments to 0.87, affording GFs with higher tensile strength (2.2 GPa) and electrical conductivity (8 × 10^5 S m^−1).[10,14] Changing spinning channel enabled the fabrication of high performance graphene belt with tensile strength of 1.9 GPa and high conductive properties (1.0 × 10^6 S m^−1; 1580 W m^−1 K^−1).[13] The uneven shrinkage during coagulation and solidification has been largely ignored, which brings unoptimized crystallization. Consequently, GF still fails the promise as a fiber material with both extraordinary mechanical and functional properties.

The assembled microstructures of macroscopic GFs are strongly dependent on conformations of graphene sheets.
Concentration of GO spinning dope is usually constrained below 1% and the extremely large volume shrinkage about 100-fold at least in the coagulation and solidification process inevitably brings chaotic wrinkles caused by the uneven compressive capillary forces. These random wrinkles, regarding as conformation disorders, inevitably lead to loose stacking and unaligned arrangement and then imperfect growth of graphitic crystallites during thermal annealing. Clearly, such conformation disorders are hard to be overcome in previous wet-spinning.

Here, we uncover a plastic state for GO fibers (GOFs) and develop a continuous plasticization spinning methodology to fully eliminate the random wrinkles and rearrange GO sheets to a compact and aligned state (Figure 1a). Intercalation of proper plasticizers turns brittle GOF into plastic one with a highest 580% enhancement of plasticity and allows GOF being plasticized and highly deformable. The wrinkled GO sheets are transformed into extended ones by stretching the optimally plasticized GOFs with critical interlayer distance ($d_c$). Subsequent thermal graphitization brings out highly crystalline GF, exhibiting align and giant graphitic crystallites consisting of large extended graphene sheets. (b,c) Digital photos of plasticization-spun GFs, showing shining surface and flexibility. (d) Overall physical characterizations of the plasticization-spun GFs at 32% SR (red line) and wet-spun nascent GFs (blue line). Scale bar, 10 mm (b,c).

Graph of stress-strain for plasticization-spun GFs and wet-spun nascent GFs. (d) Overall physical characterizations of the plasticization-spun GFs at 32% SR (red line) and wet-spun nascent GFs (blue line). Scale bar, 10 mm (b,c).

2. Results and Discussion

Thermal plasticization is a significant feature of polymers and underpins the production of high-performance polymer fibers. Inspired by this concept, we observed an elastic-plastic transition of GOF after intercalation of variable plasticizers. We detected that the intercalated GOF shows striking plasticity in contrast with the brittleness of dried GOF (Figure 2a). Nascent GOF behaves ceramic-like elastic with very limited

Figure 1. Plasticization spinning method to fabricate highly crystalline GF. a) Scheme of the plasticization stretching induced crystallization of GFs. Solid GOF shows obvious brittleness. Intercalating solvent plasticizers allows GOF being plasticized and highly deformable. The wrinkled GO sheets are transformed into extended ones by stretching the optimally plasticized GOFs with critical interlayer distance ($d_c$). Subsequent thermal graphitization brings out highly crystalline GF, exhibiting align and giant graphitic crystallites consisting of large extended graphene sheets. b,c) Digital photos of plasticization-spun GFs, showing shining surface and flexibility. d) Overall physical characterizations of the plasticization-spun GFs at 32% SR (red line) and wet-spun nascent GFs (blue line). Scale bar, 10 mm (b,c).

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Here, we uncover a plastic state for GO fibers (GOFs) and develop a continuous plasticization spinning methodology to fully eliminate the random wrinkles and rearrange GO sheets to a compact and aligned state (Figure 1a). The intercalation of proper plasticizers turns brittle GOF into plastic one with a highest 580% enhancement of plasticity and allows gradually straightening GO sheets along fibers under constant tension. Moreover, the plastic state occurs at a high weight concentration of 60–90%, largely relieving the uneven shrinkage and retaining the extended conformation in the final solid fibers. The extended graphene conformation facilitates the preferred growth of graphitic crystallites. After high-temperature graphitization, GF exhibits high density of 1.9 g cm$^{-3}$, extremely high sheet orientation degree reaching 0.97, and giant size of crystallites of 174.3 nm. The crystalline compactness and alignment of giant perfect crystallites enable GFs to achieve record overall performances, including tensile strength of 3.4 ± 0.07 GPa (the best value 3.50 GPa), electrical conductivity of 1.19±0.01) × 10^6 S m$^{-1}$, and thermal conductivity of 1480 ± 84 W m$^{-1}$ K$^{-1}$ (Figure 1d), breaking the elusive limitation of high strength and superior functionalities of conventional CFs.

Figure 2. a) Tensile test of GFs at room temperature. b) Digital photos of plasticization-spun and wet-spun nascent GFs. Scale bar, 10 mm (b,b).
tensile strain of 5% (2% elastic region and 3% plastic region). After the intercalation of plasticizers, for example, 80% acetic acid (AcOH), the deformation behavior turns to plastic with a pronounced strain limit ($\varepsilon_{\text{max}}$) of 34% (nearly unchanged 2% elastic region but largely increased plastic region of 32%). At a small strain region ($<2\%$), the stress-strain relation is almost linear but has a much lower stress due to the weakening interlayer binding. Then, at a moderate strain region (3–12%), the slope of the stress-strain curve decreases dramatically corresponding to the yielding effect caused by the flattening of GO sheets. Thereafter, at the large strain region (12–34%), the interlayer interaction and sliding occur in balance and the slope of the stress-strain curve increases considerably, behaving a strain hardening effect.

Accompanying with the plastic transition, we observed that the interlayer distance ($d$) of GOF expands from 1.0 to 3.0 nm with variable types of plasticizers intercalated saturatedly, calculated from (001) peak in X-ray diffraction spectra (XRD; Figure 2b; Figure S3b, Supporting Information). Combining the classical Lifshiz’s formula, we calculated the van der Waals interaction between two overlapped GO sheets with varied $d$. As shown in Figure 2c, the expanding $d$ weakens the interlayer attraction, thus actives the sheet sliding under tension. We estimated the tensile properties of plasticized GOF with different plasticizers intercalated (Figure 2d; Figure S3c, Supporting Information), and summarized a correlation between deformation ability (take $\varepsilon_{\text{max}}$ as a criterion) and $d$ (Figure 2e). The correlation shows that nascent GOF with $d$...
of 1.0 nm behaves brittle because of strong interlayer interaction. The increased $d$ from 1.0 to 1.2 nm (with concentration exceeding 90%) gradually lowers interlayer attraction to active the interlayer sliding, turning elastic deformation to plastic one. For $d$ larger than 2.0 nm (with concentration lower than 60%), the extremely weak interlayer attraction fails to resist massive sheet sliding, and $\epsilon_{\text{max}}$ sharply declines to 5%, similar to the case of previous direct stretching of dilute gel fiber.\textsuperscript{[10,15]} A critical interlayer distance ($d_c$) from 1.2 to 1.8 nm was found to make GOF exhibit optimally plastic deformation for continuous spinning. In this region, interlayer interaction and sheet sliding occur in balance and achieve a large plastic deformation accompanying with flattening of wrinkles.\textsuperscript{[22,23]} Different interlayer distance guided elastic-plastic transformation for GOFs corresponds with and confirms our recently reported intercalation modulated plasticization.\textsuperscript{[24]} Based on the established deformable tension-shear (DTS) chain model, we rationalized the plasticization with the concept of self-healable interlayer links (van der Waals attraction, $\pi-\pi$ interaction, and hydrogen bonding). The failure and reconstruction of interlayer links in balance contribute to the plastic strain like the dislocation gliding in metal. The optimal $d_c$ region guides the choice of proper plasticizer and plasticization range in the continuous spinning (Figure 2d,e; Figure S3c, Supporting Information). Notably, we also revealed that larger size of GO (average lateral length of 100.7 $\mu$m) results in a considerable $\epsilon_{\text{max}}$ up to 34%, 386%, and 183% higher than 7% and 12% for smaller GO sheets of 1.7 and 15.8 $\mu$m, respectively (Figure 2e; Figure S2, Supporting Information). This trend shows the plasticization process can be used to fully utilize the merits of large GO sheets, avoiding the use of small flakes to fill the wrinkled voids of giant flakes.\textsuperscript{[11]}

In the plastic state, adjacent GO sheets sliding was activated and the inevitable conformation disorders caused by coagulation and capillary shrinkage can be rearranged into flattened and extended conformation under tension (Figure 2f,g), as evidenced by real-time track of polarizing optical microscope (POM) and small-angle X-ray scattering (SAXS). POM images reveal that the plasticized GO becomes thinner and shows stronger birefringence and more regularly aligned optical textures as the tensile strain increases. SAXS patterns gradually exhibit stronger equatorial scattering patterns,\textsuperscript{[11]} reflecting improved alignment during plasticization stretching. We established a cascade plasticization stretching process in order to fabricate highly crystalline fibers (Figure 3a). The cascade stretching was set to keep the continuity of fiber spinning. We tested the chemically reduced GF (rGF) to verify such plasticization-flattening effect. Under scanning electron microscope (SEM) inspection, the diameter of rGF decreases from 14 $\mu$m of nascent fiber to 6 $\mu$m at 32% stretching ratio (SR), and the radial wrinkles on surface fade away gradually along the fiber axis (Figure 3c–f). We calculated the sheet orientation degree of these rGFs by azimuthal scanning of (002) plane in wide angle X-ray scattering patterns (WAXS; Figure 3g–j).\textsuperscript{[10,24,25]} The orientation degree of rGF is improved gradually from 0.64 of nascent rGF to 0.86 of rGF with SR of 32% (Figure 3k). The structural regulation also compacts graphene sheets in fibers with an enhanced density from 1.32 to 1.75 g cm$^{-3}$ (Figure 3k). As SR increases to 32%, the ultimate strength and electrical conductivity reach 2.25 GPa and 2.97 $\times$ 10$^4$ S m$^{-1}$, respectively, showing a great enhancement compared with those of nascent rGF (strength of 0.41 GPa, conductivity of 1.60 $\times$ 10$^4$ S m$^{-1}$; Figure 3l,m). More significantly, the rGF with SR of 32% outperforms the best ever-reported mechanical strength of annealed GF with diameter of 2 $\mu$m.\textsuperscript{[17,18]}

We further conducted thermal graphitization at 3073 K to recover atomic defects on GO sheets and generate graphitic crystallites (Figure 1a).\textsuperscript{[10,11,16–27]} Regulated alignment and compact microstructures allow preferred growth of crystallites in thermal graphitization. The sheet orientation and crystalline size, as two important parameters to evaluate the crystallinity, can be calculated from the azimuthal and radial scanning integral curves along the direction of $d$, $q_x$, and $q_y$, respectively (Figure 4a).\textsuperscript{[28–30]} As shown in Figure 4b–c, the orientation degree of GF is promoted as SR increases, increasing from 0.80 of nascent GF to 0.92 of GF at 32% SR. The (002) peak of GF with 32% SR appears at 26.54$^\circ$ ($2\theta$), higher than that of nascent GF without plasticization stretching (26.46$^\circ$), indicating a more compact structure (Figure S6b, Supporting Information).\textsuperscript{[25,31]} Full-width at half maximum (FWHM) values of (100) and (002) peaks by radial scanning at $q_x$ and $q_y$ direction in WAXS indicate the lateral length ($L_a$) and the thickness ($L_c$) of single graphitic crystallite, respectively (Figure 4d,e).\textsuperscript{[29,32]} Length of crystallite ($L_a$) of GF with 32% SR is largely promoted to 174.3 nm, 220% larger than that of nascent GF without plasticization stretching (53.9 nm), even 270% larger than previously reported typical MPP-based GF.\textsuperscript{[18]} $L_c$ remains nearly unchanged (Figure 4f). The enlarged coherence crystalline domain was further verified by the integrated intensity ratio of D-to G-band ($I_D/I_G$) in Raman spectra (887.52 nm for GF with 32% SR, 417.44 nm for nascent GF; Figure S6a, Supporting Information).\textsuperscript{[33,34]} The size for GF with 32% SR is also promoted compared to previously reported GF.\textsuperscript{[11]} The extremely large $L_a$ is mainly ascribed to the compact and aligned microstructures induced by plasticization spinning (Figure 4g).

We conducted high resolution transmission electron microscopy (HR-TEM) to observe the fiber microstructure intuitively.\textsuperscript{[29,35,36]} The graphitic crystallites of GF with 32% SR are homogeneously aligned along the fiber axis (Figure 4h). In contrast, nascent GF without plasticization stretching shows a disordered arrangement with many bifurcate wrinkles and random folds originated from the conformation disorders in nascent precursor GOFs (Figure 4k). Azimuthal scanning of (002) crystallographic facet in selected area electron diffraction (SAED) patterns on a single fiber axial slice displays an order parameter of 0.93 for GF with 32% SR, much higher than that of nascent GF without plasticization spinning (0.85; inset of Figure 4h,k).\textsuperscript{[17]} Closer examination identifies that the inner crystallite of GF with 32% SR consists of continuous graphitic lattice (length > 60 nm at least, Figure 4i). The graphene sheets align more regularly with an orientation up to 0.97 calculated from fast Fourier transformation (FFT) pattern, clearly higher than that of nascent GF without plasticization spinning (0.89, Figure 4j,m).\textsuperscript{[15]} Distinct from the continuous and integrate lattice in plasticization-spun GFs, many distortions and lattice defects, including kinks, loops, and edge dislocations are seen in nascent GF (Figure 4l,m), which are inherited from
the conformation disorders like wrinkles and crumple in precursor GOFs.

The overall higher multi-scale crystalline order and giant crystalline size of plasticization-spun GF lead to an integration of both exceptional transport and mechanical properties, overwhelming nascent GF without plasticization stretching and breaking the limit of conventional CFs in transport properties. The tensile strength and Young’s modulus of GFs are simultaneously increased with the incremental SR (Figure 5a). GF with 32% SR shows superior average strength of 3.4 GPa and Young’s modulus of 341.7 GPa, respectively. The strength of GF is 200% higher than that of nascent GF without plasticization spinning and 54% higher than that of previously reported GF at a same testing gauge of 5 mm. The high mechanical properties originate from the dense and regular arrangement of extended graphene sheets (Figure 5c), which reduces the defective grain boundaries and stress localization according to Reynolds and Sharp’s theory. Different from the size-mixing strategy to densify GFs, we used the continuous plasticization spinning method to achieve a high density of 1.9 g cm⁻³.

Figure 3. Continuous cascade plasticization spinning. a) Continuous fabrication apparatus, containing previous wet-spinning and newly introduced plasticization spinning. b) Digital photograph of GOF on drum IV. c–f) SEM images of rGFs with variable SR. For clarify, rGFs with different SR (on the four drums) are labeled as I-rGF, II-rGF, III-rGF, and IV-rGF, respectively. SR was defined as the differential speed ratio of (V₉₂–V₁)/V₁, (V₉₃–V₁)/V₁ and (V₉₄–V₁)/V₁. g–j) WAXS patterns of rGFs with variable SR. k) Orientation degree (f) and density (ρ) of rGFs at different SR. l,m) Tensile curves (l) and electrical conductivity (σ) of rGFs at variable SR. Scale bar, 10 mm (b), 5 µm (c–f), 10 nm⁻¹ (g–j).
(Figure 4c), which fully utilizes the merit of large size of graphene units. The optimized compactness and record large lateral size of graphitic crystallites, enable GF to achieve the superior electrical and thermal conductivities simultaneously. As shown in Figure 5b,d, the conductive properties of GFs increase with the enlarged crystallite size. The average electrical conductivity of GF with 32% SR is $1.19 \times 10^6$ S m$^{-1}$, surpassing that of nascent GF without plasticization stretching ($0.50 \times 10^6$ S m$^{-1}$), and even approaching half of that of graphite whisker.\[^7\] Thermal conductivity of the thin fibers is measured by a T-type method with a platinum wire serving as temperature sensor (thermal conductivity of 77.2 W m$^{-1}$ K$^{-1}$, see method in Supporting Information).\[^{26,40}\] The average thermal conductivity of GF (32% of SR) measured by the T-type method is 1480 W m$^{-1}$ K$^{-1}$, 85% higher than that of nascent GF (800 W m$^{-1}$ K$^{-1}$) and approaching 67% of that of highly oriented pyrolytic graphite (HOPG).\[^{26,40}\]

The mechanical strength and thermal/electrical conductivities of traditional carbonaceous materials are usually exclusive since their heterogeneous structure and tiny graphitic crystallites heavily reduce phonon/electron transport.\[^{26,30}\] For instance, the strength of PAN-based CF increases considerably, while their thermal/electrical conductivities almost keep stagnant below the limit of 0.1 $\times$ 10$^6$ S m$^{-1}$ (Figure 5e,f).

The crystalline compact and alignment of giant graphitic crystallites enable the first breakthrough in both mechanical and conductive properties of conventional CFs. Compared with benchmark MPP-based carbon fibers, GF shows the same level tensile strength, but 43% higher electrical conductivity.

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**Figure 4.** Crystalline structures of GFs. a) WAXS patterns of GF with optimal plasticization stretching. b) Azimuthal scan curves from WAXS. c) Orientation degree (f) and density (ρ) of GFs at different SR. For clarify, GFs with different SR (on the four drums) are labeled as I-GF, II-GF, III-GF, and IV-GF, respectively. d,e) Radial scan curves from WAXS integrated at the direction of $q_x$ (d) and $q_y$ (e). f) Relationship between the crystalline size of GFs and the sheet orientation (f) of precursor rGFs, showing that the increased stacking order of precursor fiber facilitate the preferred growth of graphitic crystallites. g) Schematic of the highly crystalline structure of GF. h–j) TEM images of plasticization stretched GFs, inset of (h) and (j) corresponding to the SAED pattern and FFT image, respectively. k–m) TEM images of nascent wet-spun GFs, inset of (k) and (m) corresponding to SAED pattern and FFT image, respectively. Scale bar, 200 nm (h), 100 nm (k), 10 nm (i,l), 2 nm (j,m), 10 nm$^{-1}$ (a), 5 nm$^{-1}$ [insets in (h), (j), (k), (m)].
and 64% higher thermal conductivity.\textsuperscript{[18]} Beyond the monotonously enhanced strength of PAN-based carbon fibers, the enhancement in overall performances of GF implies a new trend to realize high mechanical strength and extraordinary conductive function simultaneously, and directs a promising macroscopic fiber to achieve the extreme performance of graphite whisker.

### 3. Conclusion

In conclusion, the present work uncovers a plastic state of graphene oxide fibers, and develops a cascade plasticization spinning method to fabricate highly crystalline GF with superior combination of both mechanical strength and thermal/electrical conductivities. The plasticization spinning flattens the random wrinkled disorders originated from the coagulation and solidification during wet-spinning, and therefore facilitates the preferred growth of graphitic crystallites in high-temperature graphitization. The crystalline compactness, sheet ordering and giant graphitic crystallites conjoinly contribute to the outstanding integration of record mechanical and superior conductive properties. The integration of benchmark overall properties and scalable fabrication makes the GF attractive and competitive in future industrial applications. This industrially viable strategy opens an avenue to macroscopic carbonaceous fibers closely toward single crystalline graphite whisker in both mechanical and functional aspects. We believe the plastic state could extend the processing capability of graphene and the facile plasticization spinning can be generalized to guide the industrial production of fibers of graphene and other 2D sheets.

### Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.
Acknowledgements

The authors thank Dr. Xiaran Miao, Dr. Jinyou Lin, and other staffs at BL16B1 of Shanghai Synchrotron Radiation Facility (SSRF) for assistance in SAXS and WAXS characterizations. This work was supported by the National Natural Science Foundation of China (Nos. 51703194, 51803177, 51533008, 51973191, 51636002), National Key R&D Program of China (No. 2016YFA0200200), the China Postdoctoral Science Foundation (Nos. 2017M620241), Hundred Talents Program of Zhejiang University (2018020194231701/113), Key Research and Development Plan of Zhejiang Province (2018C01049), the Fundamental Research Funds for the Central Universities (No. K20200060), Foundation of National Key Laboratory on Electromagnetic Environment Effects (No. 614220504030717), and the National Postdoctoral Program for Innovative Talents (No. BX201700209).

Conflict of Interest

The authors declare no conflict of interest.

Keywords

crystalline fibers, graphene fibers, plastic state, plasticization spinning

References