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Perspective

Progress and perspective on high-strength and multifunctional carbon nanotube fibers

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Materials are foundations of human civilization. From the Stone Age to the present new material age, the history of human civilization is also a history of the development of materials. The mass production of a new generation of materials with strength, flexibility and fatigue resistance that are orders of magnitude higher than the current materials is of great importance in both science and engineering. Among various high-performance materials, lightweight and high-strength fibers and composites are a typical category of materials with strategic significance and great economic values in the fields of aerospace, national defense construction, new energy, electronic information, and intelligent sensing, etc. Among the existing high-performance fibers, carbon fibers (CFs) have excellent properties such as high strength, high modulus, high temperature resistance, high heat transfer, and low density. During the past years, CFs have become a new generation of military and civil materials which are widely used in aerospace, transportation, chemical industry, sports, and leisure products, etc. However, CFs suffer from intrinsic brittleness, poor flexibility, low shear strength, and poor toughness. In most cases, CFs are used for reinforcement in composites. The shortcomings of CFs such as low matching between CFs and resins, lack of synchronous reinforcement and toughening, difficulty of structural integration and functionalization also exist in CFs-based composites. These problems of CFs make them difficult to meet the higher requirements of high-end applications in the future.

As an allotrope of carbon, carbon nanotubes (CNTs) are endowed with unique atomic and electronic structures as well as extraordinary properties such as excellent mechanical properties, high thermal and electrical conductivity, and high carrier mobility [1,2]. CNTs are considered as one of the strongest materials with a Young's modulus over 1 TPa and a tensile strength higher than 100 GPa, which provide ideal candidates for fabricating new-generation superstrong fibers. Moreover, the mobility, on–off ratio and switching frequency of CNT-based field effect transistors (FETs) are much higher than those of silicon-based FETs. CNTs can also carry current densities up to 10^9 A/cm^2, far exceeding the upper limit of 10^6 A/cm^2 of copper wires [3], and the structure and resistance of CNTs almost remain constant when the temperature is lower than 250 °C. Besides, the thermal conductivity of single-walled CNTs (SWCNTs) is as high as 6600 W/(m K), which is three times higher than that of diamonds [2]. Moreover, CNTs can effectively shield ultraviolet corrosion, ensuring their robustness under extreme conditions. Under the same design strength, CNT-based materials can greatly reduce their weights and improve the payloads of vehicles and aircrafts. Therefore, a light, high-strength and high-toughness material system with outstanding properties and rich functions can be formed if the excellent mechanical, electrical and thermal properties of CNTs are fully utilized in the macro structures.

CNT-based materials and systems are expected to meet a wide range of practical needs in many aspects (Fig. 1). For example, in military aircrafts, CNT fibers (CNTFs) can be employed in various parts to meet the needs for high mobility, supersonic cruise and stealth, and simultaneously improve their resistance to corrosion and impact fatigue. In addition, the obvious weight-reduction effect of CNTFs can greatly increase the effective load and reduce the fuel consumption, which is promising in the development of hypersonic vehicles [4]. CNTF composites can also be used to manufacture missiles and launch vehicle engine shells. At present, almost all combustion chamber shells are wound by continuous reinforcing fiber/resin matrix. CNTFs have high tensile strength and very low coefficient of thermal expansion, as well as good adhesion with the thermal insulation layer, which render them with obvious advantages in substituting the reinforcement composites in the future. Compared with CFs, CNTFs exhibit superior specific strength, conductivity, versatility, flexibility, toughness, and fatigue resistance, showing great potential in wearable devices [5]. Wearable devices such as intelligent electronic fabrics and their integrated systems are considered as a revolution in the aspects of science and technology, while flexible fiber electrodes are urgently needed to construct high-performance fabric electronic devices. Conventional CFs can hardly meet the requirements of wearable fabric electronic devices such as high conductivity, strength, flexibility, and versatility [5]. In comparison, CNTFs perfectly meet the above requirements, which make them ideal candidates for fiber electrodes [6].

In the past 30 years, CNTs have attracted more and more attention as a rising star from both academic and industrial communities. On the one hand, the number of CNT-related journal publications and patents is increasing exponentially every year. On the other hand, the annual production of CNTs has reached thousands of tons with wide applications in many fields such as

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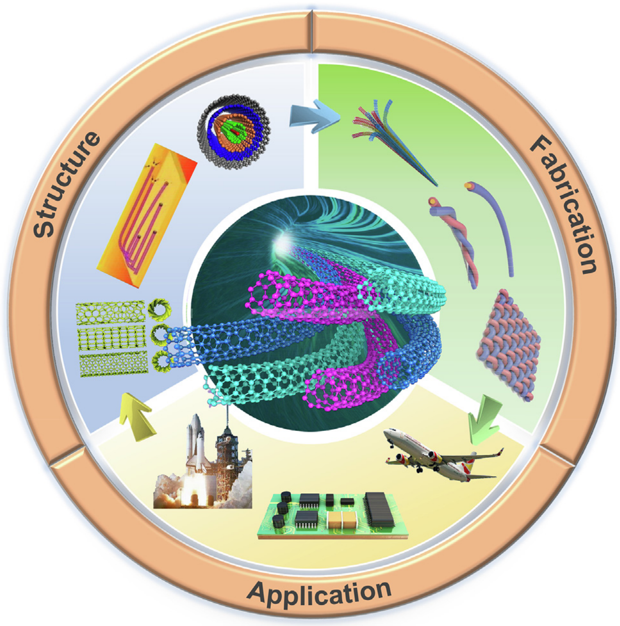

Fig. 1. (Color online) Schematic illustration of the structures, fabrications, and applications of CNT and CNTFs.

polymer composites, touch screens, conductive additives (Fig. 2). However, the lengths of these CNTs are usually within several millimeters or even micrometers. Besides, structural defects in these CNTs cause serious deterioration in their physical properties, which are much inferior to their theoretical values. For example, the tensile strength of fibers prepared from short and imperfect CNTs is only 3.76–5.53 GPa [7], which are far below the theorical values. The origin of this sharp contrast roots in the synergistic effect of the sliding and fracturing of short CNTs under van der Waals forces as well as the existence of structural defects [8]. In contrast, ultralong CNTs with length ranging from centimeters to decimeters are advantageous in the fabrication of superstrong CNTFs because of their macroscale lengths and perfect structures. In contrast, ultralong CNTs with length ranging from centimeters to decimeters are advantageous in the fabrication of superstrong CNTFs because of their macroscale lengths and perfect structures. When assembled into fibers, the interaction forces of ultralong CNTs are much larger than that of short CNTs. In comparison with the current CNTFs composed of CNTs with micrometer-scale length, it has been calculated that the strength of CNTFs made of

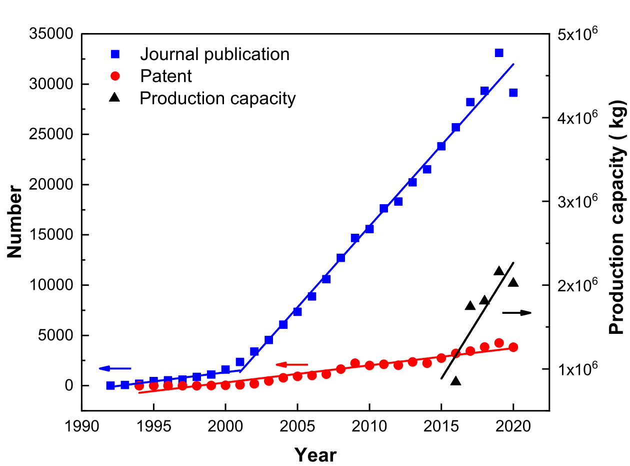

Fig. 2. (Color online) Global journal publications and patents related with CNTs, as well as China's CNT production capacity per year.

CNTs with centimeter-scale length can be greatly improved and far exceed the strength of existing fibers [9]. We also found that ultrapure semiconducting CNT arrays can be obtained when the lengths of CNTs exceed 154 mm due to the bandgap interlock mechanism, thus exhibiting great potential for the fabrication of CNT-based integrated circuits [10]. Therefore, many great breakthroughs in high-end fields are expected to be made if the controlled synthesis and mass production of ultralong CNTs with perfect structures can be realized.

The controllable synthesis of CNTs is completely different from traditional fiber materials. In essence, CNTs are self-catalytic grown by using transition metals as catalysts, carbon atoms at the end of CNTs as templates and organic carbon sources as feedstocks. It is a strong coupled process which covers chemistry, chemical engineering, and materials science. Through the topological analysis of the six membered ring formed by tubular sp^2 carbon, combined with the understanding on the templating self-catalysis, researchers utilized the higher energy barrier for forming defects according to the topological protection mechanism [1,11–13]. In this way, the defect concentration was successfully reduced to the level of 10^{-11}, facilitating the synthesis of 65 cm long defect-free CNTs [10]. Defect-free CNTs showed a revolutionary improvement of 15 times in the strength, 3 times in the modulus, and 40 times in the toughness compared with CFs and spider silks. Moreover, according to our recent studies, defect-free CNTs can achieve the highest fatigue resistance and flexibility, and the tensile strength of the obtained CNT bundles is also one order of magnitude higher than that of state-of-the-art CFs [8,14].

The key to developing high-strength multifunctional CNTFs is to study the controllable synthesis, basic physical properties of defect-free CNTs and their assembly approaches. Generally, nanomaterials face serious problems of "size effect" in their scale-up process, which means that their performance degrades drastically when forming macroscale assemblies [15]. The size effect of materials is reflected in the following aspects. Firstly, the defects of materials at the atomic level have significant effects on their macro performance. Due to the principle of entropy increase, bulk materials will always have point defects or line defects, the crack propagation of which induces the size effect. However, as a typical kind of low dimensional materials with very small diameters (generally only a few nanometers), CNTs can be macroscopically free of defects because they are all composed of covalent bonds of surface atoms and have the topological protection of tubular six membered ring structures. This characteristic of CNTs also renders them with ultra-high strength and toughness. Secondly, the interactions between CNTs can be very complicated. For example, after the formation of CNT bundles, the stress between the tubes will be uneven even individual CNTs are defect-free, resulting in serious stress concentration on a small portion of CNTs in the bundles [8]. Therefore, when the number of CNTs in a bundle increases, the macroscale strength decreases exponentially. Third, due to the limitation of CNT length, the stress concentration caused by the connection and kink of CNTs will also bring serious size effect in CNT bundles and fibers. Finally, when forming composites with polymers, due to their great differences in strength, modulus and orientation, the mechanical, electrical and thermal properties also have big differences. Researchers have made great efforts in improving the synthesis of CNTFs and the preparation of superstrong materials through orientation and densification. CNTFs with strength up to 5.53 GPa, as well as good toughness, flexibility and conductivity were successfully prepared [7].

How to overcome the "size effect" and realize the intrinsic excellent properties of CNTs is an important problem to be solved in the fabrication of CNTFs. Researches on the preparation and mechanical properties of CNTFs have witnessed rapid progress in recent years. Various CNT spinning methods have been proposed and improved, and CNTFs with tensile strength comparable to the best CFs at present were prepared [16]. However, even so, the mechanical properties of reported CNTFs are still far from that of individual CNTs, showing an obvious "size effect". Therefore, it is a key scientific problem to investigate the assembly law of CNTs at different scales and establish the relationship between fabrication process, structure, and properties of CNTFs, thus paving the way for their large-scale applications. In addition, the effects of the structure and defects in CNTFs are diverse, and their interfacial interactions are complex. Moreover, the mechanism for the initiation, propagation, and failure of microcracks in CNTFs-reinforced composites is not clear. Therefore, it is necessary to further investigate the strengthening, toughening and functionality of CNTF composites. Assisted by large-scale computational simulation, theoretical modeling and characterization analysis, the interfacial structures, effects of defects and failure mechanisms of CNTFs-reinforced composites are expected to be systematically studied.

In addition, how to maintain the intrinsic excellent properties of CNTs when assembled into aggregates is the most significant and difficult problem for CNTFs. To narrow the gap between nanostructures and macroscopic properties, there are some important aspects for researchers to consider, i.e., the growth mechanism of individual CNTs, the assembling law of CNTs, the functionalization of CNTFs, and the formation of CNT composites. Firstly, the growth mechanism of CNTs needs further and deeper investigations to achieve the controllable synthesis and performance improvement of individual CNTs. As mentioned above, once the defect-free ultralong CNTs are successfully mass produced, high-performance CNTFs will far exceed the current commercial fibers not only in mechanical strength but in electrical, thermal performance, etc., which is expected to fill the gap of high performance fibers in civilian and military. It is necessary to investigate the growth mechanism of CNTs, and provide guidelines for the controlled synthesis of CNTs in terms of wall number, diameter, chirality, defect concentration and length, etc. In this way, the properties of individual CNTs are expected to be largely improved, facilitating the downstream applications. Secondly, in addition to improving the quality of individual CNTs, the interaction and the assembling of CNT monomers are also of crucial importance, because they establish linkages between nanostructures and macrostructures. The alignment, entanglement and interactions between CNTs have dominant effects on the mechanical, electrical and thermal behavior of CNTFs. Therefore, a clearer understanding and the corresponding intensification of the assembling process are urgently needed to make CNTFs fully exhibit the advantages of individual CNTs. Thirdly, CNTFs are promising candidates for the building blocks of flexible electronic textiles due to their high conductivity, high strength, high flexibility, etc. More importantly, they are easy to be functionalized. However, introducing functional components while maintaining the intrinsic properties of CNTFs is still challenging. The high curvature of the surface of fibers makes it difficult to apply the conventional coating processes which are suitable for planar devices. Thus, the interfacial interactions between CNTs and functional components need to be further studied and regulated. Fourthly, it has been proved that CNTs are effective additives to enhance the mechanical, electrical and thermal properties of composites. However, the dispersion and orientation of CNTs in certain polymer matrices are hard to control, which limits the reinforcement effect greatly. The effect of morphology and intertube topology of CNTs on the crosslinking and interaction at the CNT/polymer interfaces requires further investigation.

In summary, faced with the great demand for superstrong materials in high-end fields such as military and aerospace, CNT-based materials show great advantages not only in strength but also in toughness, elongation and conductivity, etc. The controllable synthesis of CNT-based materials with excellent properties that are comparable with individual CNTs is of great significance to realize their large-scale applications in numerous cutting-edge fields.

Conflict of interest

The authors declare that they have no conflict of interest.

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