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Design, Fabrication and Application of Multi-Scale, Multi-Functional Nanostructured Carbon Fibers

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Abstract

To further improve and upgrade the existing functions of carbon fibers, and to endow the carbon fiber with new and desired functions, the most effective and economic way is to create nanostructures on the carbon fiber surface. The carbon fibers with nanostructures grown on the surface, or namely nanostructured carbon fibers, not only maintain the intrinsic high strength, light weight, high thermal conductivity of carbon fiber, but also obtain significant functional enhancements in mechanical properties, interfacial bonding and electrocatalytic property. Different kinds of nanostructures, such as nanoparticles, nanorods, nanotubes, nanosheets, and nanoflowers, are controllably grown on the surface of carbon fibers by using various kinds of techniques, including chemical vapor deposition (CVD), laser ablation, microwave treatment, and hydrothermal process. These multi-scale, multifunctional nanostructured carbon fibers not only add new and interesting branches to the carbon fiber family, but also pave the way for the application of carbon fibers in next-generation fiber-reinforced composite, energy storage device and green energy production.

Keywords: surface growth, carbon fiber, nanostructures, fiber-reinforced composite, electrocatalyst

1. Introduction

Owning to its high mechanical strength, light weight and one-dimensional morphology, carbon fiber has become one of the most important materials in fabricating structural components and load-bearing parts, and has found wide-spread applications from the fields of automotive, sports, to aircrafts and aerospace shuttles. Perceived by its name, carbon fiber is composed of the elemental carbon (C). Different from graphite, which is composed of sheets of carbon

atoms (graphene sheets) that parallelly stack on each other, the carbon fibers are composed of graphene sheets that twisted, folded and crumbled upon each other. Therefore, carbon fibers would have extremely high tensile strength and stiffness as compared to graphite. Carbon fibers are majorly produced from the precursors such as polyacrylonitrile (PAN), rayon and petroleum pitch [1]. In a typical process, the precursors are spun and drawn to form filament yarns, which are subsequently subject to the pre-oxidation, thermal carbonization and graphitization processes. After the thermal carbonization process, the precursor filament yarns are converted to carbon filament yarns with high carbon contents (~92–99%). The carbon filament yarns produced from the carbonization process (1500–2000°C) generally exhibit high tensile strength while the ones produced from the graphitization process (2500–3000°C) generally exhibit high elastic modulus [2].

Due to its high mechanical strength, high modulus, thermal conductivity and low thermal expansion, carbon fibers are widely used in the high technology sectors, such as aerospace and nuclear engineering, where high performance under high damping, high temperature and corrosive environment is required [3]. However, in general engineering sectors and transportation, the application of carbon fiber is restrained by the cost and production rates, and it only appears in limited parts of the products, where high strength and light weight are needed. The final properties of carbon fibers are highly dependent on their precursors and different types of carbon fiber can be produced based on the specific requirements of application. For example, the carbon fiber produced from PAN has the highest tensile strength (Table 1), which is suitable for the high technology applications. On the other, the carbon fiber produced from cellulose may have lower tensile strength accompanied with low cost, which is suitable for general engineering applications (Table 2) [4].

The properties of carbon fibers can be further improved by the growth of nanostructured materials on their surfaces, a process commonly known as “whiskerization” [5–7]. Techniques such as chemical vapor deposition, hydrothermal process and electrochemical deposition are usually employed to accomplish the nanostructure growth [8–10]. During the growth process, the nanostructures are directly formed on the surface layer of the carbon fibers, either through the pre-deposited “seed layer” or hydrophobic interaction. After the growth process, the as-grown nanostructures and the carbon fiber substrates integrate and form free-standing, binder-free multi-scale composites. Depending on the properties of the as-grown nanostructures, the applied functions of carbon fiber can be greatly enhanced and extended.

Precursor	Tensile strength (GPa)	Tensile modulus (GPa)	Elongation at break (%)
PAN	2.5-7.0	250-400	0.6-2.5
Mesophase pitch	1.5-3.5	200-800	0.3-0.9
Rayon	≈ 1.0	≈ 50	≈ 2.5

Table 1. Mechanical properties of PAN, pitch and rayon based carbon fibers [3].

Precursor Material	Diameter	Strength [GPa]	Modulus [GPa]	Elongation [%]
lyocell	7.5	0.9		
rayon	7.5	0.81		
lyocell		0.49	37.6	1.4
lyocell filled with 5 wt% carbon black		0.57	48.3	1.2
rayon		0.82	79.2	
lyocell		0.94	99.7	
lyocell		1.07	96.6	
lyocell		0.40		
rayon "Ural"		0.5–1.2	100	
hydrated cellulose		1.65	97	
rayon		0.944	54.3	1.76
rayon		1.535	59.8	2.57
viscose		0.6	50	
rayon				
cellulosic fiber		2–4		
cellulose fiber		0.2–0.44		3.0
sisal fiber		0.8	25	

Table 2. Mechanical properties of cellulose based carbon fibers [4].

For example, growth of carbon nanotubes or zinc oxide nanowires on the carbon fiber surface can significantly increase the tensile strength (133%) and interfacial strength (113%) of the fiber-reinforced composite prepared by using these carbon fibers [11, 12]. By growing metal oxide or metal dichalcogenide nanostructures on carbon fiber surface, the electrochemical catalytic and capacitive properties of carbon fibers can be substantially enhanced [13, 14]. Upon integrating the intrinsic high electrical and thermal conductivity, high mechanical strength and chemical inertness of carbon fibers with the nanostructured materials of high electrochemical activity, ideal bi-functional (anode and cathode) electrodes for metal-air batteries and water-splitting cells can be readily realized, which further extends the applications of carbon fiber to energy storage and green energy [15, 16]. This chapter will focus on the state-of-the-art design and growth of functional nanostructures on carbon fiber surface, as well as their advanced applications.

2. Nanostructures grown on carbon fiber for fiber-reinforced composites

Due to its excellent mechanical, thermal and chemical properties, carbon fibers are widely used for the fabrication of fiber-reinforced composites (FRC), forming high-performance structures and components for high-technology applications. However, the most frequent occurring cases for the failure of FRC known as fiber pull-out and delamination are caused by the internally weak bonding between the fibers and the polymeric matrix [17, 18]. In this regard, growth of secondary nanostructures on the surface of carbon fibers to improve the interfacial bonding

between the fibers and matrix has been proposed [19, 20]. In order to obtain the desired enhancement in the interfacial bonding strength, three main factors should be considered, including: (i) the as-grown nanostructures should have intrinsically good mechanical properties, proper size range and high surface area, which can significantly increase the interfacial area between the fiber and matrix, as well as providing good anchoring strength; (ii) the nanostructures should be directly grown on the surface of carbon fibers to avoid the involvement of binders, as binders could affect the mechanical strength of the final composites; (iii) the process of growth should not deteriorate the intrinsic mechanical properties of carbon fibers.

2.1. Growth of nanocarbons

Due to their intrinsic affinity to the surface of carbon fibers, carbon nanomaterials (nanocarbons) have been grown on carbon fiber for the FRC application. For example, carbon nanotubes (CNTs) grown on carbon fibers are speculated to improve the interfacial bonding in FRC due to the high mechanical strength, high surface area and good substrate adhesion [21]. Extensive research efforts have been devoted to grow CNTs on carbon fibers while the diameter, length and crystallinity of the as-grown CNTs can be effectively controlled [22–25]. Techniques of chemical vapor deposition (CVD) are widely applied to grow CNTs on carbon fiber surface (**Figure 1**). In a typical process, the carbon fibers are firstly cleaned and desized in organic solvents by sonication, and then immersed in the catalyst solution at elevated temperature for absorbing and loading of the metal catalysts. Metals, such as iron (Fe), nickel (Ni), cobalt (Co), are the major catalysts used for the growth of CNTs [27, 28]. After the immersion and the subsequent drying process, the surface of carbon fiber is densely loaded with small metal particles, as shown in **Figure 2**. Afterwards, the metal-loaded carbon fibers are placed in a quartz tube furnace, which are subsequently heated in the presence of hydrogen (H_2) and carbon source mixed stream (e.g., benzene, ethylene, acetylene) to accomplish the CNT growth. The flow rate of total gas streams is typically in the range between 100 mL min^{-1} and 300 mL min^{-1} , and inert gas protection is required during the heating and cooling steps.

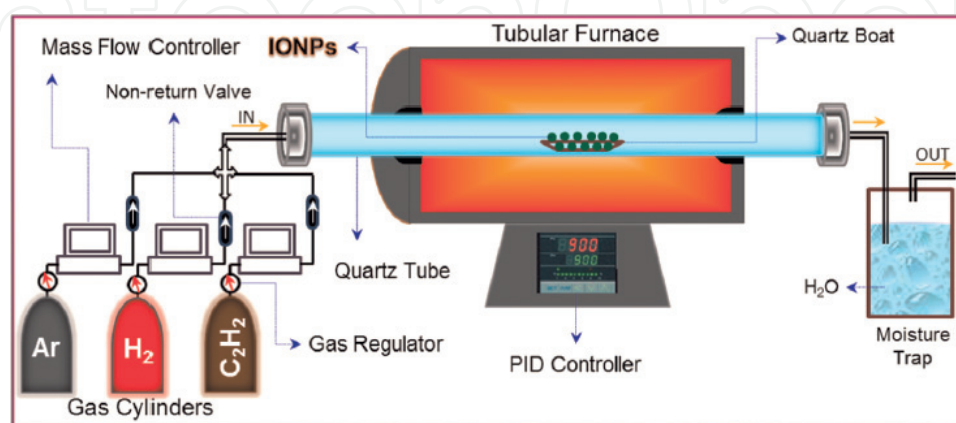


Figure 1. Schematic illustration of the CVD process for growing CNTs [26].

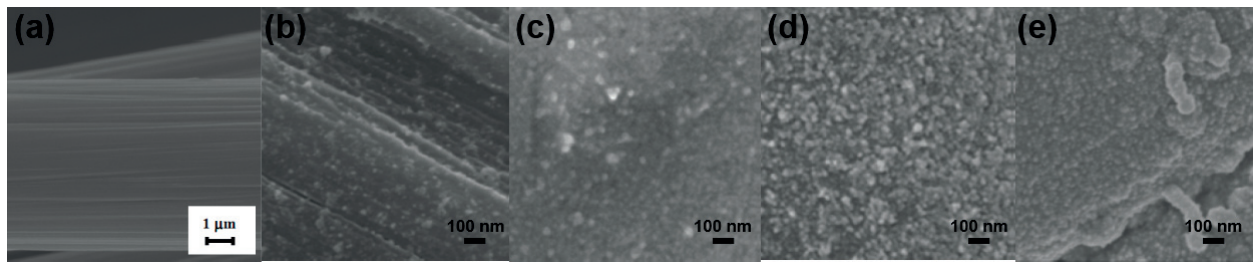


Figure 2. Scanning electron microscopy (SEM) images of (a) bare carbon fiber surface [11] and (b-c) Ni particle-loaded carbon fiber surface with increasing concentrations of the catalyst solution [24].

The as-grown CNTs exhibit long and curved shapes which wrapped around the longitudinal axis of the carbon fibers randomly, as shown in **Figure 3**. The morphology of the as-grown CNTs can be controlled by a wide-range of parameters including types of catalyst, catalyst concentration, gas flow rate, growth time and temperature. A brief summary of the relationship between the carbon fiber morphology and these parameters is provided in **Table 3**. Amongst these parameters, the catalyst concentration is speculated to play a major role since all the morphological related parameters (e.g., diameter, length, density) can be effectively tuned by it (**Figure 4**). It should be noted that there exists a proper range for tuning the growth parameters of CNTs, and beyond this range CNTs may not be properly grown [30]. Other than CNTs, carbon nanofibers (CNFs) can also be grown on the surface of carbon fiber by using the same chemical vapor deposition (CVD) procedures [31–33]. Different from CNTs, the CNFs is characterized as long nanofibers with solid core, and they would generally have higher aspect ratios than CNTs. It is speculated that by increasing the time of CVD the CNTs can be further grown into CNFs, as shown in **Figure 5** [34].

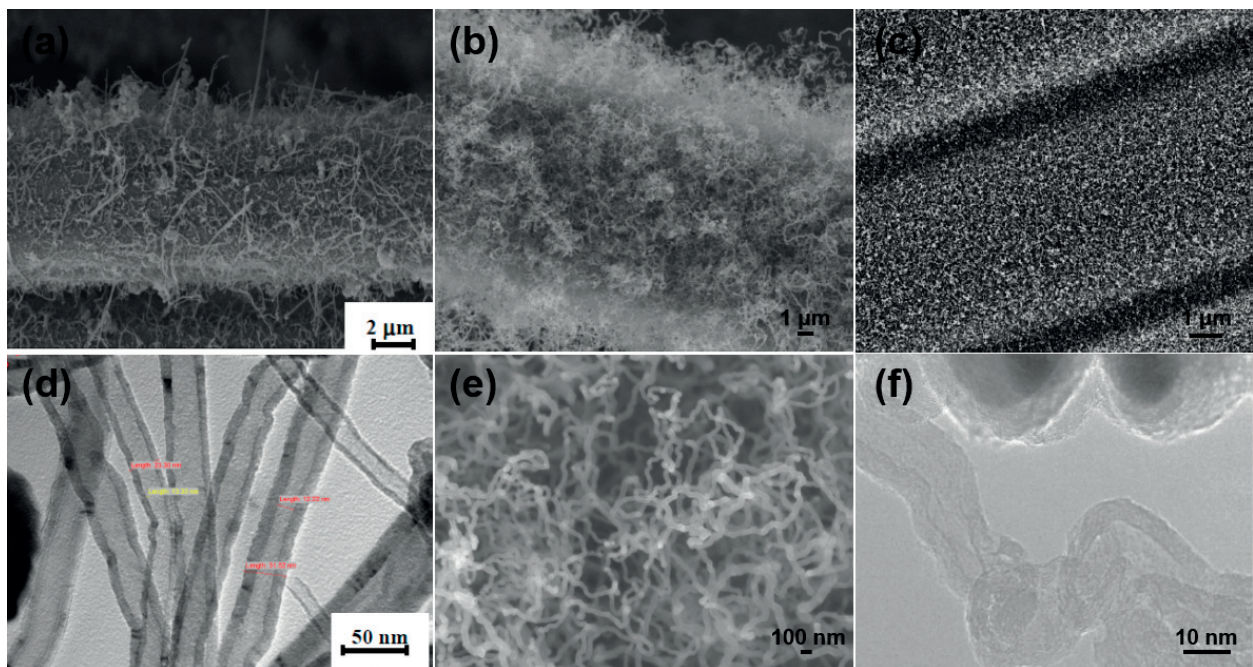


Figure 3. SEM and TEM images of CNTs grown on carbon fiber by using (a, d) Fe based catalyst [11], (b, e) Co based catalyst [22], and (c, f) Ni based catalyst [29].

Parameters	Diameter	Length	Thickness
Catalyst concentration	+	+	+
Temperature	-	+	-
Time	+	+	+
Flow rate	+	+	+

Table 3. Correlation between the morphology of CNTs and growth conditions. (+) represents in direct proportion while (–) represents in inverse proportion.

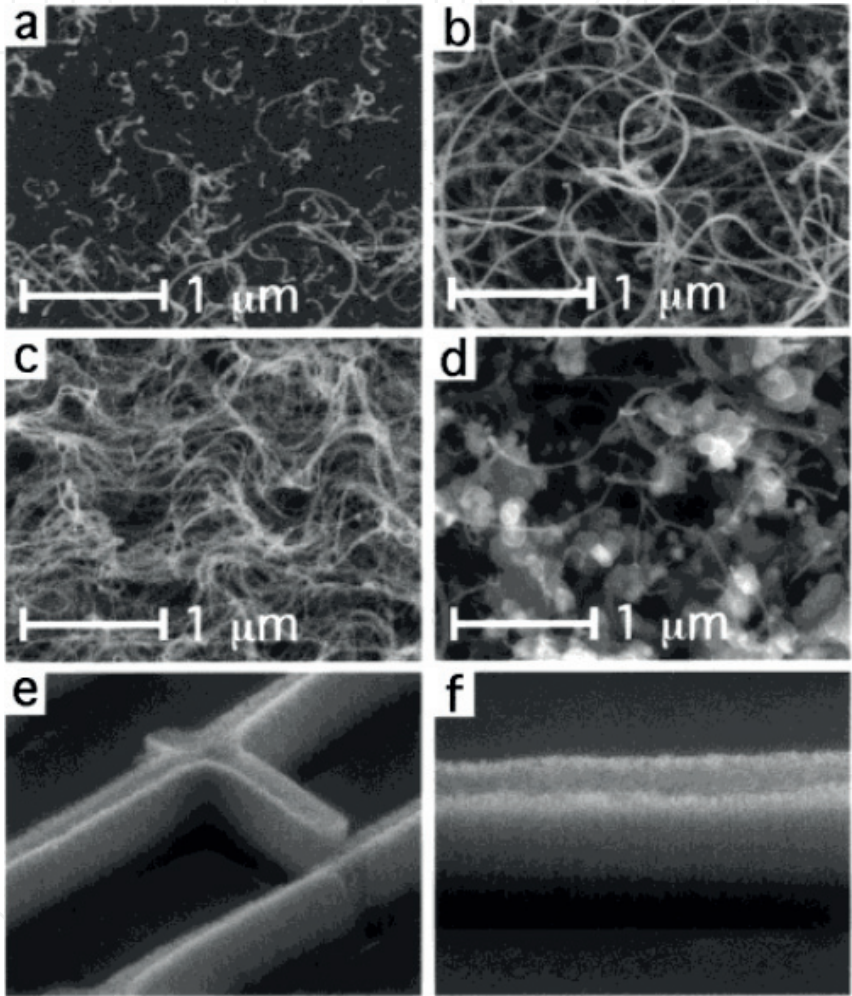


Figure 4. Pattern films of CNTs grown by increasing catalyst concentrations: (a) 10 mM, (b) 25 mM, (c) 40 mM, (d) 70 mM; (e, f) 50 mM $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. Aligned CNTs grown perpendicular to the substrate surface can be observed in (e) and (f) with a width of 10 μm and height of 20 μm [30].

2.2. Growth of nanostructured metal oxides

Besides CNT and CNFs, metal oxide nanostructures are also grown on carbon fibers to improve their interfacial bonding strength, respectively [35–37]. The hydrothermal method is widely used to grow metal oxide nanostructures, as illustrated in **Figure 6**. Compared with the growth of nanocarbons, growing metal oxide nanostructures on carbon fibers by the

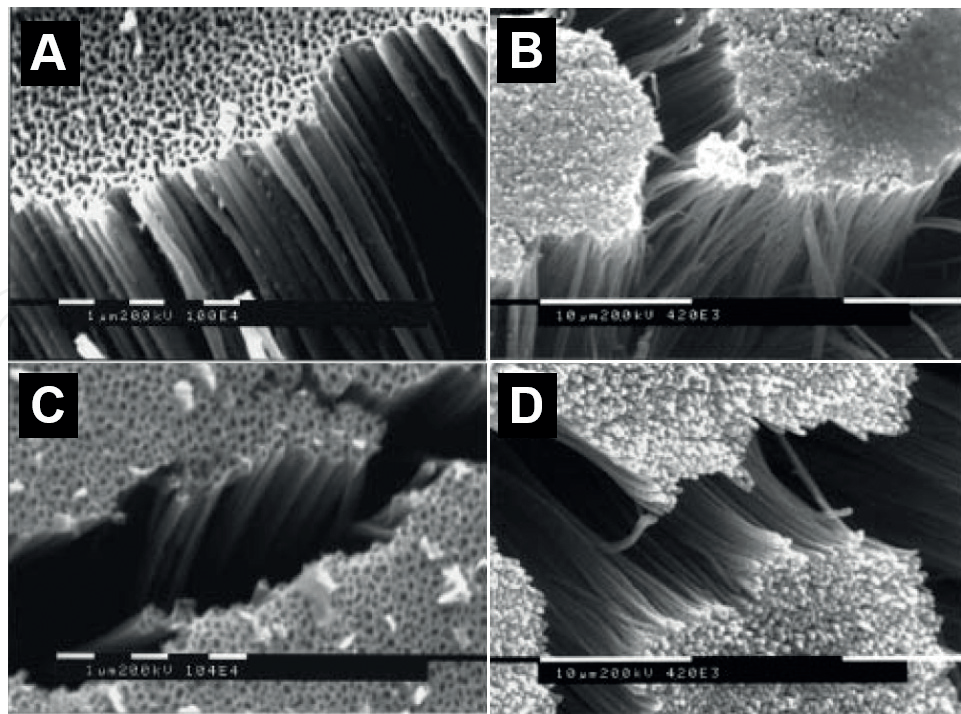


Figure 5. SEM images of the CVD-grown (a, C) CNTs and (B, D) CNFs obtained from 10 min and 40 min at 900°C, respectively [34].

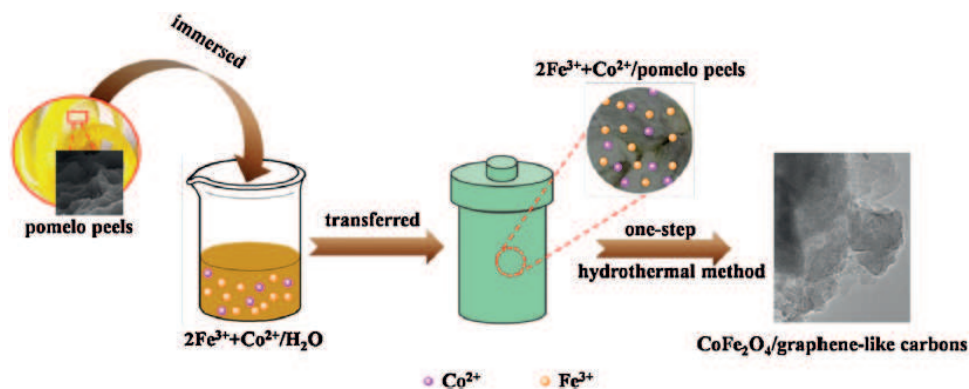


Figure 6. Schematic illustration of a typical hydrothermal process that used for the synthesis of metal oxide [42].

hydrothermal method may obtain the advantages including: (i) higher degree of morphological control over the as-grown nanostructures can be achieved on the carbon fiber surface. In other words, higher structural uniformity and higher growth density can be readily achieved for the as-grown metal oxide nanostructures; (ii) the growth process of metal oxides is simpler and requires less instrumentation, the material and energy consumption are also less comparing with the thermal CVD process; (iii) by using the same growth protocol, different types of nanostructured metal oxides can be grown on the surface of carbon fibers. However, CNTs and CNFs grown by thermal CVD may still possess the pros including: (i) higher theoretically predicted improvement in the interfacial strength for FRC; (ii) higher surface area of the as-grown nanostructures, and (iii) better affinity or adhesion to the carbon fiber substrate [38].

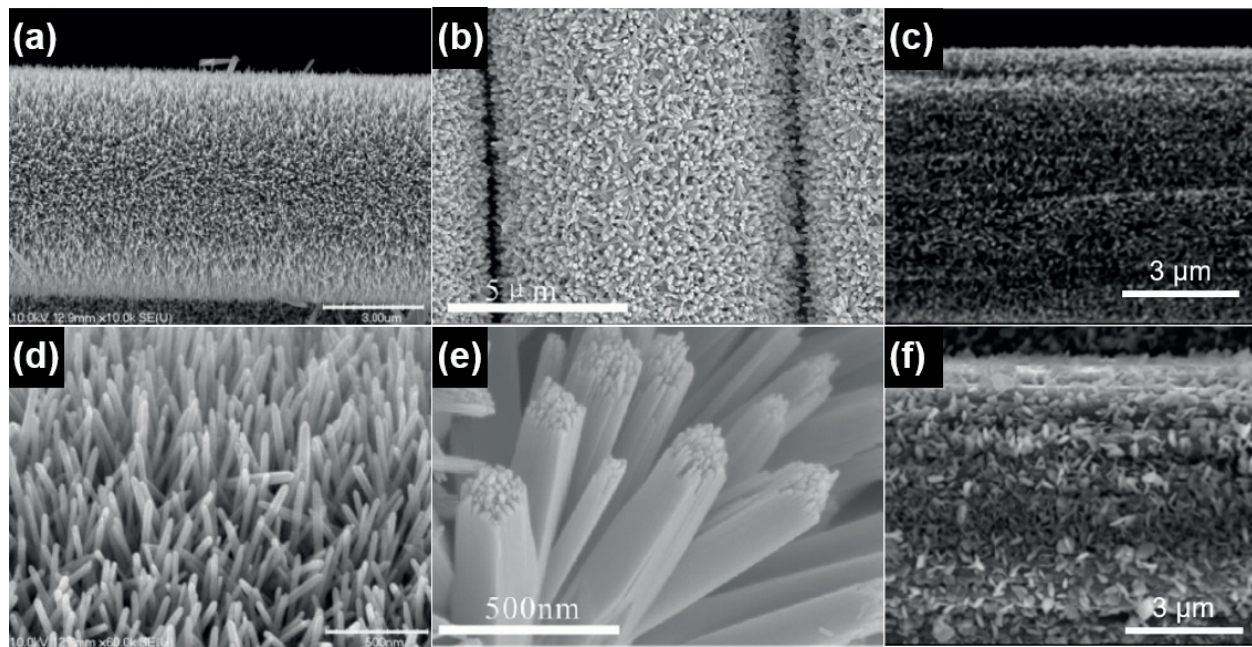


Figure 7. SEM images of metal oxide nanostructures grown on carbon fiber by using hydrothermal method: (a, d) ZnO nanowires, (b, e) TiO₂ nanorods and (c, f) CuO nanowires [12, 36, 37]. The CuO nanowires in (c) were synthesized from 10 mM seeding solution while the nanowires in (f) were synthesized from 50 mM seeding solution.

Given the remarkable advantages of growing metal oxide nanostructures for FRC application, extensive research efforts have been made to investigate their growth process as well as their functional performance in FRC [39–41].

During the hydrothermal process, the metal oxide “seeds” are firstly deposited on the surface of carbon fiber by immersing the carbon fibers in the solution of metal salts. Afterwards, the seed-loaded carbon fibers are annealed at elevated temperature in atmospheric pressure, in order to improve the adhesion between the seeds and the fibers. Then the treated carbon fibers are immersed in a “growth solution” which contains the metal salts and organic polyamines (e.g., hexamethylenetetramine, HMTA). The growth process is then proceeded by heating the solution in a glass beaker at elevated temperature on a hotplate. Or a stainless-steel autoclave can be used if higher temperature and pressure are needed. The zinc oxide (ZnO) and copper oxide (CuO) nanowires, titanium dioxide (TiO₂) nanorods synthesized by using the hydrothermal method are shown in **Figure 7**. Similar to the growth of nanocarbons, structural control over the as-grown metal oxide nanostructures can be achieved by tuning the concentration of the “seeding solution,” loading quantity of the metal oxide “seeds,” as well as the time of growth (**Figure 7c** and **f**).

2.3. Mechanical properties of carbon fibers with surface-grown nanostructures

The carbon fibers with carbon or metal oxide nanostructures grown on the surface are eventually subject to the mechanical testing, in order to reveal their functional performance in enhancing the interfacial bonding strength within the FRC and the mechanical strength of the whole FRC.

Materials	Tensile strength (MPa)	Modulus (GPa)	Interfacial shear strength (MPa)	Maximum increment (%)	Reference
CNT-CF	27	1.07		133% in tensile strength	[11]
ZnO NW		3.34	33.87	113% in shear strength	[12]
CNF	23.9–24.8	0.75–0.79			[33]
CNT				17% in fracture toughness	[23]
CuO NW				42.8% in tensile strength	[36]
TiO ₂ NR	200.5			45% in tensile strength	[37]
ZnO NW				209.5% in loss factor	[43]
ZnO NR				50% in loss factor	[44]
CNT				300% in conductivity	[45]
CNT				510% in conductivity	[46]
CNT				56% in loss factor	[47]
CNT				69% decrease of crack propagation	[48]
CNT			18.1	45% in shear strength	[49]
CNT				127% in impact energy dissipation	[50]
CNT				30% in shear strength	[51]
SiO ₂ NP			52	44% in shear strength	[52]
Graphene				173% in shear strength	[53]

Table 4. Mechanical properties of carbon fiber with different nanostructured materials grown on its surface. NW refers to nanowires while NR and NP refer to nanorods and nanoparticles, respectively. The “shear strength” shown in table refers to interfacial shear strength.

In a typical process, the carbon fibers are chopped into smaller fibers with less dimensions (length ≤ 2 mm), which are subsequently mixed or blended with the matrix materials, such as epoxy and polypropylene. The mixtures are then cast in a mold with applied pressure and subsequently solidified by either curing or compression molding to form the FRC. Mechanical testing, including tensile strength, modulus, shear strength and compressive strength, are applied to the nanostructured carbon fiber reinforced polymer composites (CFRC) and the representative results are shown in **Table 4**. It is found that the as-grown CNTs and CNFs are capable of increasing the mechanical strength of the whole CFRC to a great extent, while the metal oxide nanowires can significantly improve the interfacial strength between the carbon fiber and polymer matrix.

3. Nanostructures grown on carbon fibers for energy storage and green energy electrodes

Similar to the growth of metal oxides, secondary nanostructures composed of the compounds of transition metals and non-metals can also be grown on the surface of carbon fiber to extend

its range of application to energy storage and green energy electrodes. The intrinsically high electrical and thermal conductivity, chemical inertness and flexibility make carbon fiber an ideal electrode substrate for the fabrication of high-performance hybrid electrodes that are capable of catalyzing targeted electrochemical reactions in harsh conditions effectively, efficiently and stably. The state-of-the-art research has been focused on using the carbon fiber hybrid electrodes in supercapacitors, lithium-ion batteries and water-splitting [54–56]. To accomplish the requirements for these applications, various types of hybrid catalysts have been grown on the surface of carbon fibers either by electrochemical deposition or electrodeless deposition. However, most of these materials can be categorized as the hybrids of transition metals and non-metals, including MnO_2 , MoS_2 , NiP, FeS_2 , CoSe_2 , NiCo_2S_4 , etc., [54–59]. Similar to the growth of metal oxides, the hydrothermal method is widely adapted for growing the hybrid electrode catalysts. Other methods, such as in-situ redox process and thermal annealing, are also used to grow the hybrid catalysts [60, 61]. However, in order to obtain hybrid catalysts with desired elemental composition, additional steps such as vulcanization, selenization and phosphorization are required. The representative SEM images of the hybrid catalysts grown on carbon fibers are shown in **Figure 8**.

Based on their elemental composition, the applications of the as-grown hybrid catalysts can be categorized as supercapacitor, lithium-ion battery and water-splitting. For example, the metal oxides (e.g., MnO_2) are well-suited for supercapacitors and metal dichalcogenides (e.g., MoS_2) with layered structures are suitable for lithium-ion batteries, while metal phosphorus based catalysts (e.g., NiP) are suitable for water splitting. The carbon fiber-based hybrid electrodes demonstrate high electrocatalytic performance in these applications, as shown in **Table 5**.

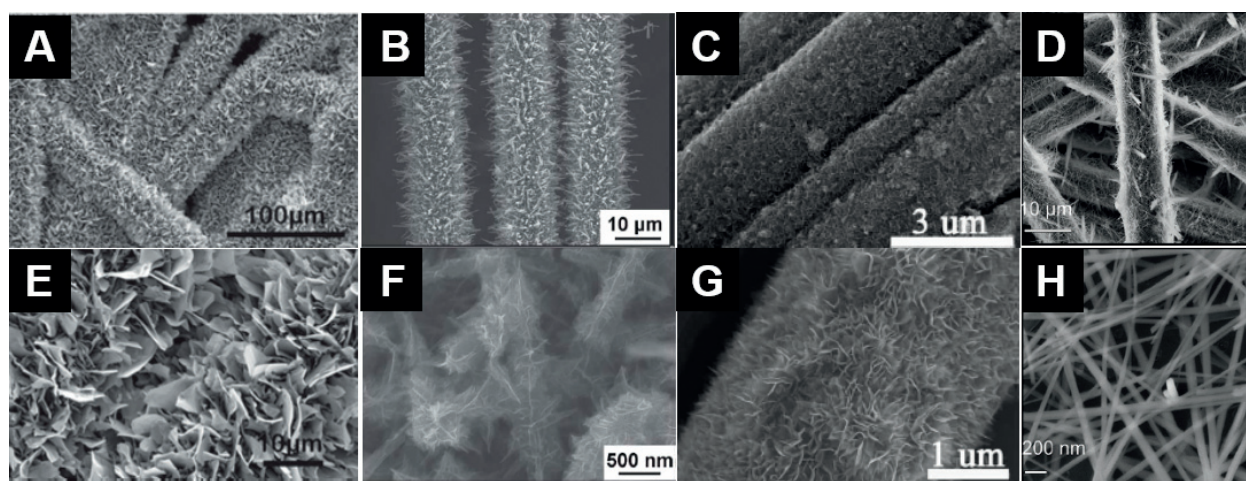


Figure 8. SEM and magnified images of hybrid nanostructured catalysts on the surface of carbon fibers: (A, E) NiP nanoflakes; [56] (B, F) whisker-like MnO_2 arrays; [62] (C, G) MoS_2 nanosheets; [61] (D, H) Co_3O_4 nanonet [63].

Materials	Applications	Performance	Reference
NiCo ₂ S ₄ nanotube	Supercapacitor	Discharge areal capacitance of 2.86 F cm ⁻² at 4 mA cm ⁻²	[54]
FeS ₂	Lithium battery	Discharge density of 1300 Wh kg ⁻¹	[55]
NiP	Water splitting	250 mV OP for 100 mA cm ⁻² cathodic current density; 0.3 V OP for OER current of 50.4 mA cm ⁻²	[56]
PPy-MnO ₂	Supercapacitor	69.3 F cm ⁻³ at 0.1 A cm ⁻³ ; 6.16 × 10 ⁻³ Wh cm ⁻³ at 0.04 W cm ⁻³	[57]
MoS ₂ nanofilm	Water splitting	216 mV OP for 100 mA cm ⁻² cathodic current density	[58]
CoSe ₂ NP	Water splitting	180 mV OP for 100 mA cm ⁻² cathodic current density	[59]
MnO ₂	Supercapacitor	Volume capacitance of 2.5 F cm ⁻³ ; energy density of 2.2 × 10 ⁻⁴ Wh cm ⁻³	[60]
MoS ₂ NS	Lithium-ion battery	Discharge capacity of 971 mA h g ⁻¹	[61]
MnO ₂ arrays	Supercapacitor	Capacitance of 274.1 F g ⁻¹ at 0.1 A g ⁻¹	[62]
Co ₃ O ₄ nanonet	Supercapacitor	Capacitance of 1124 F g ⁻¹ at 25.34 A g ⁻¹	[63]
MnO ₂	Supercapacitor	Capacitance of 467 F g ⁻¹ at 1 A g ⁻¹	[64]
CuO NF	Supercapacitor	Capacitance of 839.9 F g ⁻¹ at 1 mV s ⁻¹ ; energy density of 10.05 Wh kg ⁻¹ and power density of 1798.5 W kg ⁻¹	[65]
Nickel copper hydroxide	Supercapacitor	770 F g ⁻¹ at 5 mA cm ⁻² ; energy density of 33 Wh kg ⁻¹ at a power density of 170 W kg ⁻¹	[41]
WP NR	Water splitting	230 mV OP for 100 mA cm ⁻² cathodic current density	[66]

Table 5. Applications and performance of different hybrid nanostructured catalysts grown on carbon fiber. OP refers to overpotential, while NS refers to nanosheets, NF refers to nanoflowers.

4. Conclusion and future work

The growth of nanostructured materials on the surface of carbon fibers can significantly improve the interfacial mechanisms of the carbon fiber-based composites as well as introducing additional advanced functions to the carbon fiber substrate. The growth of one dimensional nanocarbons and nanostructured metal oxides on carbon fibers results in greatly enhanced tensile strength, interfacial shear strength, impact resistance and damping when being used in fiber reinforced composites. On the other, by growing hybrid nanostructured catalysts on carbon fibers, high performance electrodes with outstanding electrocatalytic properties can be facilely prepared, which further extends the applications of carbon fiber-based electrodes to supercapacitors, lithium-ion batteries and water splitting cells. In order to further improve the functional performance of the carbon fibers grown with surface nanostructures, future research in the related fields should pay attention to tailor the morphology and composition, as well as the orientation, spacing and thickness of the as-grown nanostructure.

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Conflict of interest

The authors declare no conflict of interest.

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