Carbon and Boron Nitride Nanotubes: Structure, Property and Fabrication

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As an interesting and important material, carbon nanotube (CNT) and boron nitride nanotube (BNNT) have been widely used in various applications such as electrical conductor, thermal management, catalyst, sensing, energy harvest and storage, tissue engineering, drug delivery, bio-imaging and cancer therapy. The special size, geometry, aspect ratio, chemical composition and electronic structure endow them the unique properties. Nanotube basics for CNT and BNNT will be covered in this review, such as structures, properties and synthesis methods.

Keywords: Nanotube; CNT; BNNT

Received 20 December 2018, **Accepted** 13 January 2019

DOI: 10.30919/esmm5f199

1. Introduction

Nanotubes are hollow fibers at the nanoscale. Since the discovery of carbon nanotube (CNT) in late 1990s,¹ nanotubes have drawn great interests for its high aspect ratio, high specific surface area and nano-size dependent properties. As a consequence, nanotubes such as CNT, boron nitride nanotube (BNNT), titanium dioxide (TiO₂), zinc oxide (ZnO) nanotube and other nanotubes are widely studied in environmental remediation, catalyst application,^{2,5} energy harvest and storage,⁶⁻¹⁰ sensors,^{11, 12} bio-medical/tissue engineering,¹³⁻¹⁶ optoelectric application,¹⁷ conductive and thermal management applications^{18, 19} and many other fields.²⁰

As one of the most important nanotubes, CNT has attracted both academia and industry interests for its special size and electronic structure. CNT has been used as nano-electronic element to continue the nearly ended Moore's Law. However, three major problems are retarding CNT for applications: large scale production, manipulation and chirality separation.^{21, 22} Up to date, the producing capability of CNT for most companies is about a ton per year, which is extremely limiting its application. The chirality separation is the key for CNT to be used as

nano-electronic components. Therefore, researchers are looking forward to multi-functional and hybrid composites rather than nano-electronics. The special multi-functional properties are contributed by either composition or structure. For example, hybrid and hierarchical structures.

In this review, we will go through the CNT and BNNT in three sections: structure, property and synthesis methods. In the first section, basic structures of different nanotubes are illustrated. Properties of nanotubes are discussed on mechanical, electrical and thermal aspects. Synthesis method defines the structure/property, which is essential for nanotubes' application. In this case, we emphasized conventional and emerging fabrication methods in the third section. Modification and functionalization of nanotubes methods are discussed as well. Nanotube based hierarchical structures are introduced in the fourth section. Building hierarchical structure with various synthesis methods is an important approach in designing multifunctional and meta- materials.

2. Structure and property of nanotubes

2.1 Structure of nanotubes

CNT is the most typical model to illustrate the structure of nanotubes. As shown in Fig. 1, CNT can be considered as rolled graphene sheet. The electronic structure of formed CNT differs by rolling orientation. And the corresponding CNT is noted as armchair or zig-zag. The chirality notation is represented by a vector pair (n, m) which is also called chiral vector (Fig. 1c). The chirality becomes one of the most important characteristic for single wall carbon nanotube (SWCNT). The armchair CNT (n, n) is metallic (Fig. 1a). However, the zigzag CNT (n,0) (Fig. 1b) is quasi-metallic. When n-m is a multiple of 3 (n≠m, nm≠0), the SWCNT is also quasi-metallic. All other CNT are semiconductive.²³ The match of electronic structure between different walls can change its electronic property as well.²⁴ The structural stress of CNT always exists. Normally, the smaller diameter, the larger internal stress will be. However, when researchers are seeking smaller CNT, they successfully synthesized stable and small CNT with an inner diameter of 0.4 nm.^{25, 26} CNTs can be classified in two main categories: single wall carbon nanotube (SWCNT)²⁷ and multi-wall carbon

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Fig. 1 Structure and chirality of CNT. (a) Armchair assembly of SWCNT; (b) Zig-zag conformation of SWCNT; (c) Chirality of CNT. Transmittance electron microscope (TEM) image of SWCNTs; (d) (18, 8) SWCNT; (e) (28, 0) zigzag SWCNT; (f) higher magnification image of (e) (Warner *et al.* 2011 Adapted with permission of Nature Springer);²⁷ (g) TEM image of MWCNT shows the loss of five walls (Yuzvinsky *et al.* 2005 Adapted with permission of AIP publishing).²⁸

Fig. 2 Structure of (a) BNNT and (b) h-BN; (c) Chiral vector of MoS_2 nanotubes; (d) armchair MoS_2 nanotube; (e) Zig-zag MoS_2 nanotube;³⁰ (f) Layer structure of MoS_2 .

Fig. 3 Structure of BPNT³². (a) Top view of single layer black phosphorus sheet (SLBP); (b) Zigzag-view of SLBP; (c) Armchair-view of SLBP; (e) Armchair BPNT; (f) Zig-zag BPNT.

Fig. 4 TEM image of VGCNF. (a) detailed wall structure; (b) Stacked cup structure; (c) dimensions in the stacked cup structure.³⁶

nanotube (MWCNT)²⁸ (Fig. 1d, e, f, g). Some studies are using double wall CNT (DWCNT) for functionalization of CNT.²⁹ The outer wall can provide the location for chemical bonding and the inner wall supports the structure. Sorting different CNTs is a significant topic due to the difference of CNT's electronic property. This difference is also preventing CNT from being used as nano-electronics in large scale production. Most researches are using chromatography related methods which are based on the weak interaction between electron density with chromate fillers.²¹ The other method is using a special polymer which can wrap the semiconductive CNT for separation.²²

By alternatively replacing the carbon atoms in CNT with boron and nitrogen atoms, we can get boron nitride nanotube (BNNT). As it has an identical structure with CNT, BNNT shows a similar outstanding mechanical property. BNNT is also called white CNT due to its white color. Different from full carbon structure, boron nitride (BN) has a much better stability in oxygen (Fig. 2a), especially at high temperature. This allows BN material to be excellent candidate for thermal management and thermal ablation applications. Hexagonal BN (h-BN) nanomaterials, such as BN nanosheet and BNNT, have been widely used as fillers to improve thermal conductivity of polymers. Besides, the

electronic structure formed by boron and nitrogen makes BNNT a wide bandgap insulator (~ 5.5 eV).

Black phosphorus is new graphite like 2D semi-conductive material. By using exfoliation methods,³¹ phosphorene (single layer black phosphorus: SLBP) can be obtained. As a result, black phosphorus nanotube (BPNT) is expected.³² However, different from CNT, the BPNT has 1 layer of phosphorus atom but aligned in 2 cylindrical planes (Fig. 3). Similarly, MoS₂ nanotube consists of two molybdenum layers and one sulfur layer (Fig. 2d, 2e and 2f).³⁰ Besides, there is a large group of 2-dimensional materials can be rolled up to nanotubes.³³⁻³⁵

Besides these well aligned walls, there is another kind of nanotube consist of stacked Dixie shaped structure.^{36, 37} Different from the vertical aligned walls in SWCNT and MWCNT, its wall consists of wrapped graphene layers (Fig. 4). Such a material has a hollow core and the diameter is about 200 nm. As a result, this material can be called either MWCNT or vapor grown carbon nanofiber (VGCNF).³⁶ Due to its large diameter, high crystallinity and high roughness surface, the VGCNF is a wonderful material for mechanical reinforcement and electrical conductive nanofiller.

2.2 Properties of nanotubes: mechanical, thermal and electrical

The conductivity of metallic conductive CNT is higher than most metals such as copper.³⁸ Such a high conductivity attribute to the ballistic transportation of electrons. The conductivity of CNTs depends on ambient temperature and isotope composition as well.³⁹ Similar as the transportation of electron, the special structure of CNT also allows ballistic transportation of phonon. This result CNT has an excellent thermal conductivity and Young's modulus. Both theoretical calculation and experimental results show CNT has the highest mechanical property. For SWCNT, the tubular graphene structure consists of sp² hybrid C-C bond only. On the other hand, the chirality of CNT defines its mechanical property along its axis as well. As a result, the tensile strength of CNT ranges from 10 GPa to 150 GPa and the Young's modulus ranges from 0.2 TPa to 5 TPa. However, we have to notice that the different measurement techniques lead to different results.

Meanwhile, BNNT shares a similar structure with CNT, the hexagonal-tubular structure. On the other hand, boron and nitrogen are the two closest elements to carbon. As a result, the structural property of BNNT and CNT is about to be similar. The Young's modulus of BNNT was measured to be around 500 GPa to 1.2 TPa.⁴⁰ However, the

theoretical value is about 700 to 900 GPa.⁴⁰ It seems these measured and simulated values are in a smaller range compare to the CNT's values. This might because the CNT is discovered at an earlier time. With the development of experimental techniques and modeling accuracy, the obtained values of BNNT are more accurate.

Another advantage of CNT and BNNT is their low density. Theoretically, the specific strength of CNT and BNNT is approximately 300 times of high-carbon steel. Pop and Kim measured the thermal conductivity of CNT is up to 3500 W/m K which value approaches to the theoretical one. On the other hand, thermal conductivity of CNT and BNNT are as high as 300 W/m K and isotope affects this value as well.³⁹ Common polymers have low thermal conductivity of 0.1~0.35 W/m K.²⁰ As a result, CNT and BNNT are widely added into polymers for enhancing the thermal conductivity of polymers. Besides chirality difference, such a huge properties' variance also origins from defects of the structure leading to another shared problem for nanotubes: when a single nanotube is being used, the connection between nanotube structure (two tube ends) and the connected material is always the weak point. This weak point might be a nanotube-metal bonding, or strong internal stress from distorted bonds. Another interesting property of CNT is that the tube can deform to flat belt. Such a behavior allows CNT to be used for collision absorption applications.⁷

BNNT has an additional advantage for its high atmosphere stability. The BNNT can stand at least 800 C in the air while the CNT can only bear 400 C. This advantage makes BNNT an outstanding candidate for thermal protection and ablation applications such as re-entry vehicle coating. However, the alkaline solution can dissolve BN materials easily including BNNT and boron nitride nano-sheets (BNNS). These special chemical properties are contributed by the B-N bonding while the B-N bonding can be easily dissociated into B-OH group and N-H group. However, B-N bonding is hard to be oxidized directly into B-O and N-O bond without a proper catalyst. This special B-N bonding also brings BNNT a big band gap. BNNT are usually treated as wide band gap or insulating material due to its big band gap of 5.5 eV. With any kind of doping, the band gap is going to be reduced. Additional information is summarized in later sections.

3. Synthesis methods

There are two main synthesis methods for nanomaterials, bottom-up and top-down. The bottom-up method is an assembling process; however

Fig. 5 Instrumentation for arc discharge method and laser ablation method.

the top-down method is about etching or losing of material. Synthesis process is the most important procedure. It defines the morphology of product nanostructure and further controls properties of application. Several conventional and emerging nanotube synthesis methods and technologies are introduced in this section. Modification methods for nanotubes are discussed as well.

3.1 Arc discharge and Laser ablation

CNT was found accidentally in the carbon soot of using arc discharge method for carbon filament and fullerene.¹ Arc discharge method usually consists of two graphitic electrodes which are very close to each other (Fig. 5, left). By applying a 100 A current, the arc will be generated and the temperature could reach 2000 K. During this process, the graphitic anode sublimates, then atomic carbon migrates to the cathode, and deposits onto the cathode. This process produces a large amount of carbon soot. Inert gas such as helium and argon are generally used. Metals are used as catalysts, such as Fe, Ni, Co, B and so on. By tuning the arc conditions (electrode distance, inert gas, gas pressure, current and catalyst), the product ranges from SWCNT, MWCNT, C_{60} , carbon nanofiber, amorphous carbon to carbon soot. However, CNT is more like a byproduct since this process produces too many other products.

Laser ablation is the other energetic method for the production of carbon nanomaterials which was firstly introduced by Smalley's group in 1995.⁴⁰ The basic setting of laser ablation consists of high energy laser, graphitic target, and collector (Fig. 5 right). The setup is usually set in

low pressure (500 Torr) inert gas quartz tube at high temperature (~ 1200 C).⁴⁰ This process greatly improved the yield of CNT from 30% of arc discharge method to 70%. Besides the laser parameters (such as wavenumber, photon density, and pulse duration/frequency), other parameters such as furnace temperature, inert gas pressure, target composition, collector temperature, target-collector distance are also important. For example, using Nd: YAG laser shoot a Co/Ni-graphite composite target at 1200 C could produce a large amount of SWCNT.^{40, 41} Arc-plasma⁴² and laser ablation⁴³ were used to produce silicon nanotubes (SiNT) as well. However, for cost-effective fabrication of SiNT, template method is the most widely used. Template synthesis of SiNT will be introduced in the later section.

3.2 Plasma torch

Plasma is a useful tool for preparing nanomaterials, such as thin film, nanoparticle and of course nanotubes.^{44, 45} During the process, the carbon source is heated to a plasma state in a designed reactor and carbonaceous products are deposited on a target. The plasma can be induced either by microwave or radio frequency torch. The diameter of CNTs produced from plasma method is usually very low.⁴⁶ The large amount of carbon soot around CNTs is hard to be removed, which means the purification of this CNT kind is hard. The advantage of this method is the production rate is high. Keun Su Kim *et al.* could produce SWCNT at a rate of 100 g/h with a yield of 40 wt%.⁴⁷ Energy consumption of plasma methods is lower than the arc discharge method

Fig. 6 CNT CVD instrumentation (a) and growth mechanism (b).

and laser ablation method. Currently, plasma methods are usually applied to assist other methods such as the CVD method.

3.3 Chemical vapor deposition (CVD)

Compare to arc discharge, laser ablation and plasmonic methods, CVD method allows a lower synthesis temperature (400 C ~ 900 C), which means a lower energy consumption and simpler instrumentation. With this convenience, CVD becomes the most widely used method to produce CNTs and also some other nanomaterials. CVD methods can produce various nanotubes, such as SWCNT, MWCNT, VGCNF, BNNT etc. A typical CVD instrumentation consists of a gas source, furnace/reactor, and substrate (Fig. 6a). Key parameters are chemical composition of the gas source, flow rate, furnace/reactor temperature/pressure, substrate kind, catalyst composition, and deposition duration. Besides, by changing gas source composition, catalyst, temperature, etc., other nano-materials can simply be synthesized easily, such as carbon coil,⁴⁸ graphene,⁴⁹ nanodiamond⁵⁰ and so on. As shown in Fig. 6a, CVD method also allows the growth of nanotube to be well controlled on the substrate (orientation, location, length, etc.) which makes CNT based nano-electronics become more possible.

The CVD process, as shown in Fig. 6b, there are two mechanisms: tip growth and bottom growth. Both of them consist of 4 steps: decomposition of carbon contained gas source on catalysts, the formation of carbide, the growth of nanotube, deactivation of catalyst. Before synthesis, catalyst (transition metal salt solution, such as $\text{Ni}(\text{NO}_3)_2$) is usually cast or coated on the substrate (graphite, copper, mica, silicon wafer, etc.). The metal salt decomposes and turns into metallic carbide when touches the carbon source. When the CVD process begins, carbon contained gas source decomposes on the surface of deposit onto catalyst. However, the catalyst can also be contained in the carbon source. For example, ferrocene is an iron contained organic molecule which can be carbon source and catalyst at the same time.⁵¹⁻⁵³ After the carbon source decomposed, the carbon atoms join the carbide and form the initial tube structure. With more carbon atoms depositing, the tube can grow longer and longer. However, catalysts' activity and lifetime become the limitation for CNT's length. Sumio Iijima *et al.*^{54, 55} enhanced its activity and lifetime by introducing water into the gas source. Rufan *et al.* applied the principle of Schulz-Flory distribution for polymerization on the growth of CNT.⁵⁶ They interpreted the relationship between catalyst activity probability and CNT length, an ultra-long CNT (550 mm) was synthesized. On the other hand, the catalyst particle size defines the diameter of CNT. During the growth process, the carbon source self-pyrolyzed and graphitized which may produce amorphous carbon surround the growing CNT. However,

Christoph *et al.* found the existence of amorphous carbon surrounds may not stop the activity of catalytic decomposition and graphitization.⁵⁷

The catalyst can be deposited on the substrate, floating in gas source, and supported on the carrier. Al_2O_3 , SiO_2 , MgO , zeolite nanoporous particles (Fig. 7a) were used as carriers to support the catalyst nanoparticles. By mixing catalyst precursor solution with these porous materials, after a calcination process, the precursor is transformed into oxide nanoparticles. During the CVD process, the oxide nanoparticle will be reduced by gaseous chemicals (H_2 , NH_3 , etc.) firstly. However, due to the use of supporting material, the purity of CNT is limited. Sol-gel and aerogel approaches are used to prepare high specific surface area supports and which can improve the total yield significantly. Cassell *et al.* prepared SWCNT using a metal nanoparticle on $\text{SiO}_2/\text{Al}_2\text{O}_3$ sol-gel hybrid material with a yield of 30 wt.%.⁵⁸ Su *et al.* improved the yield by 300% with a modified aerogel method.⁵⁹

Metal-free CVD is becoming focused recently because the metallic species is a big disadvantage for CNT to be used in bio-medical, tissue engineering applications. In some cases, metal free CVD does not require a further purification process. Bilu *et al.* used scratched Si/SiO_2 wafer as a substrate to synthesis SWCNT.^{60, 61} In his experiment, the scratched edge becomes the nucleation site. Nanodiamond particle was also used for metal-free CVD.^{62, 63} A thin layer of nanodiamond was spread on a graphite substrate at 600 C. Ethanol was used as gaseous carbon source for CVD at 850 C. Isolated CNT was obtained while the nanodiamond particle remained the same compared to its original state. However, the CNT growth mechanism in this procedure is still unclear. Another study suggests oxides might be able to activate the growth of CNT.^{64, 65} Another study shows the CNT can continuously grow even after the metallic catalyst being capsuled inside the tube, which means the metallic catalyst only initiate the growth process.⁶⁶ This concept is different from major studies, more in situ observation and theoretical studies are needed.

Production of CNT with CVD has many derivations, such as plasma enhanced CVD (PECVD),^{67, 68} water-assisted CVD,^{54, 55, 69} camphor based CVD^{69, 70} and HiPco CVD (Fig. 7b),^{71, 72} hot filament CVD.⁷³ For example, the PECVD coupled plasma torch (Fig. 7c) and CVD methods. By using high frequency (radio frequency range) source, the electron in gas precursors can be heated to more than 10,000 K while the atom remains hundreds of Kelvin. Such a hot electron can significantly enhance the dissociation reaction and reduce processing temperature. Most of the derivations are developed for massive production purpose.^{47, 49, 54, 55, 58, 74-78} When researchers face so many kinds of CNTs, apparently, a standard for CNT and the related product is needed. Parameters such as inner wall diameter, outer wall diameter,

Fig. 7 (a) TEM images showing CNT by CVD with Fe, Co/Zelite catalyst;⁷⁰ (b) SWCNT bundle from HiPco method (Reprinted with permission from AIP publishing);⁷² (c) CNT forest for chip application from PECVD method.⁶⁸

length, impurity percentage and impurity composition should be included. A standardized CNT regulation is very important for its commercialization.

BNNT was also produced with arc discharge method and laser ablation method^{79, 80} after Marvin Cohen theoretically proofed its existence in 1994.⁸¹ However, it was in 2010s, plasma and CVD related methods were successfully developed for large volume production of BNNT (Fig. 8c). Such as RF plasma torch, induce-coupled plasma (ICP),⁴⁴ pressurized vapor/condenser method (PVC)⁸² and PECVD. The synthesis principle of BNNT is similar to CNT which consist of gas decomposition and tube growth. However, the raw material varies a lot. In the production of CNT, the gas source is always the carbon source. In the production of BNNT, the gas source can be either borazine ($B_3N_3H_6$) or NH_3 . When $B_3N_3H_6$ is used, the substrate catalyst might be nickel boride nanoparticle.⁸³ Other precursor systems are developed due to the high cost of $B_3N_3H_6$, such as the most common boron/metal oxide powder mixture which is also called boron oxide CVD (BOCVD)⁸⁴⁻⁸⁶. The metal here can be Fe, Mg, Li, and Ni.⁸⁷ Solid boron reacts with MgO and forms B_2O_2 when the temperature is over 1200 C in which B_2O_2 exists as a gas. The other gas source, such as NH_3 , decomposes into N_2 and H_2 at such high temperature. Then, H_2 reacts with the oxygen from B_2O_2 to form H_2O ; N_2 reacts with boron to form BNNT.^{87, 88} Of course, BNNT can be produced as well with gaseous B_xH_y and NH_3 at lower reaction temperature with increasing cost on instrumentation and procedure complexity.⁷⁴

Other nanotubes made from CVD methods such as germanium nanotube⁸⁹ (Fig. 8a, 9b) and silicon nanotube (SiNT) share a similar synthesis principle as CNT and BNNT.⁹⁰ Especially, Germanium is a member of group IV element which can form hydrogen contained compound easily such as methane, acetylene, silane, germane and stannane. As a result, the existence of corresponding nanotubes is predictable.⁹¹ Because these nanotubes are less studied, currently, only electrical properties were explored in experiments or simulations.⁹¹

3.4 Electrochemical methods

CNT is less made from electrochemical methods. MWCNT can be prepared from electrolysis of carbon electrode in molten $LiCl$.⁹² The experiment was carried at 600 C. Ren *et al.* used low melting point eutectics lithium carbonate ($LiNaKCO_3$; *m.p.* 399 C) as electrolytes, CO_2 as the carbon source, Ni as electrode and catalyst prepared long carbon nanofiber. Derek Fray explored a lot on molten salt based electrochemical synthesis of carbon nanostructures.^{76, 77, 93, 94} He found that graphene sheets are peeled off from the graphitic anode in the electrolysis process. Then, the graphene sheets are rolled up in the molten salt and the MWCNT forms at the interface of the cathode and the molten salt. Other carbon nanostructures form at the same time due to the etching and disintegration of graphene sheets/flakes.⁷⁷

3.5 Template methods

Although CNT, BNNT, SiNT and Germanium nanotube are usually made from CVD methods, template methods will work as well.^{89, 90} Template method is always companying with other methods such as CVD, sputtering, physical/chemical coating, electrospinning, pyrolysis and electrochemical method. Generally, template methods can be classified into 3 categories: bottom-up, top-down and transformation.

- (1) Coat target material on a cylindrical and removable core (Fig. 9a).
 - (2) By etching the material in a designed pattern, nanotube arrays can be created (Fig. 9b). For example, using the focused ion beam (FIB) etch a silicon substrate.
 - (3) Transform organic nanostructures to carbonaceous nanotube by pyrolysis or sintering (Fig. 9c). For example, pyrolyzing of core-shell electrospun nanofiber can produce ultra-long carbonaceous nanotube.⁹⁵
- By all means, the template method has to be coupled with other deposition or growth methods. It's the special geometry of template allow the formation of the nanotube to be easier. Also, the formed nanotube is usually highly uniform and aligned compare to CVD, arc discharge, laser ablation, and hydrothermal method.

Fig. 8 TEM images of Ni-NR assisted Ge nanotubes showing control of wall thickness by CVD at (a) 330 C for 0.5 h; (b) 330 C for 1 h; (c) Large scale production of BNNT. TEM image of double wall BNNT (d) and 4-walled BNNT; (e) SEM image of cloth like BNNT sheet. Reprinted (adapted) with permission from ref.^{45, 89} Copyright (2011) American Chemical Society.

Fig. 9 Template methods. (a) Coat the nanowire; (b) anodization and coating method; (c) pyrolysis of polymer nanotube precursor.

3.6 Hydrothermal method

In short, the hydrothermal method can be described as 'stew'. Many nanostructures can be synthesized from this method, such as quantum dot, nanoparticle, nanowire, nanotube and gel. However, the main problem is yield and purification for the fabrication of nanotube.⁹⁶ Gogotsi *et al.* synthesized MWCNT in aqueous environment.⁹⁷ They put polyethylene, water, and nickel catalyst into a reactor at 700 C - 800 C under 60 MPa -100 MPa. Under this a hydrothermal condition, the water is in the supercritical state and which may promote the carbonization reaction. Firstly, the C-H will be dissolved in the supercritical water. With an increase of pressure, the solubility of carbon decreases and then carbon deposits onto the surface of catalyst particles. Gogotsi *et al.* also suggest that their experiment may explain why CNT can be found in carbonaceous rocks in nature.⁹⁸

3.7. Mechanical method

Both CNT⁹⁹ and BNNT^{78, 99, 100} can be prepared by mechanical methods as well, for example, ball milling. However, the nanotubes cannot be formed with just only the ball milling process. A post-treatment of high-temperature annealing is the key for the growth of nanotubes. Precursors, gas and room temperature are the only requirements for the ball milling process. The process can take up to 150 hours. After the milling, the material anneals between 700 K ~ 2000 K for 6 h. Although the mechanism is still not well understood, it suggests nucleation of nanotubes occurs in the milling process and the nanotube grows during annealing.⁹⁹ Yu *et al.* compared the effect of annealing gas. They found

that the BNNT grows without a catalyst in NH_3 . The growth process is slow but the resulting nanotube has fewer defects and the wall is very thin (~7 nm in diameter with 4 walls). However, in N_2 or $\text{N}_2\text{-NH}_3$ ambient with catalyst, the BNNT grows fast with lots of defect structures such as bamboo, Dixie cup shapes (20 nm ~ 150 nm in diameter).¹⁰⁰ On the other hand, Zhu *et al.* produced BNNT fuzzy SiC fiber using powder boron with N_2 .¹⁰¹ Their study focused on the formation mechanism of two types of BNNT: tip growth and bottom growth. They found that the flat wall BNNT is from tip growth mechanism and the bamboo-bubble wall BNNT comes from bottom growth mechanism. And the difference is driven by the interaction stress difference between the catalyst nanoparticle and the substrate surface. Since the mechanism on the growth of nanotubes from ball milling method is still unclear, a further experimental and theoretical study on morphology and chemical composition of milled graphite are needed.^{102, 103}

3.8 Modification of nanotubes

The aim of modification of nanotubes is either improving their processing ability or functionalization for special application. By modification, nanotubes can be functionalized with additional chemical groups or nanostructure. Modifying nanotubes into nanostructures is considered to be hierarchization of nanotubes which has been discussed in the previous section. Also, non-covalent functionalization is not involved. In this section, we are going to focus on chemical modification and functionalization.

Chemical functionalization of CNT has been widely studied since

Fig. 10 Modification methods for CNT. (a) chemical routes; (b) cycloaddition;¹²² (c) asymmetric functionalization (Reproduced from Ref. ¹²² with permission from The Royal Society of Chemistry); (d) TEM image of Pt nanotube deposited onto the nanotube tip. Reprinted (adapted) with permission from ref. ^{13, 116, 118} Copyright (2005) American Chemical Society.)

its discovery. For example, amidation,¹⁰⁴ amination,¹⁰⁵ esterification,^{106,107} metallization,^{14,108} thiolation (Fig. 10a),^{109,110} cycloaddition (Fig. 10b),¹³ and halogenation are well studied.^{111,112} The easiest method is converting the carbon-carbon structure into carboxylic acid, hydroxyl group and epoxy group.^{113,114} There are many methods to induce the oxygen contained organic groups, for example, ozonolysis treatment and aggressive acid method. The caps of CNT can be removed effectively by a mixture of concentrated sulfuric acid and nitric acid. In order to create the curvature of CNT cap, pentagonal carbon rings always exist. However, this pentagonal carbon ring is much less stable comparing with the hexagonal one. As a result, oxygen contained groups can be easily bonded to carbon atoms on the caps. Both experimental and theoretical studies on oxidation mechanism of CNT show the carbon reacts quickly with nitronium and forms carbonyl group and then transforms into phenol or carboxylic groups.^{75,115} At a lower temperature, the reaction occurs at the defective place which is the cap; while, the reaction can be initiated at any place at a higher temperature. Usually, the functionalization is processed in aqueous dispersion or gas phase. Dai *et al.* developed several methods for asymmetric functionalization.¹¹⁶⁻¹¹⁸ The methods are using compacted and well aligned CNT forests. By immersing one side of the aligned CNT into a chemical solution, the

CNT tip can be functionalized (Fig. 10c).¹¹⁶ Masking is another method to obtain asymmetrically functionalized CNT (Fig. 10d).^{117,118} High energy methods can be used for oxidation of CNT as well. For example, the ball mill and high energy radiation method were studied.¹¹⁹⁻¹²¹ The advantage of high energy methods is that a large amount of materials can be modified and the method can also be applied to other materials such as graphene, h-BN (hexagonal boron nitride), BNNT, etc.

Acids are usually used to initialize the functionalization of CNT. However, BN is very stable against acids. On the other hand, most BNNTs are produced by using NH_3 as a reactant from the CVD method the edge of BNNT remains a large amount of N-H groups. In this case, reactions based on the N-H group are used for functionalization of BNNT. For example, Zhi *et al.* used stearoyl chloride to modify BNNT based on the reaction between $-(\text{C}=\text{O})-\text{Cl}$ group and N-H group.¹²³ Surface-initiated atom transfer radical polymerization (ATRP) method was used to attach various polymer (polystyrene: PS, polymethylmethacrylate: PMMA) on the surface of BNNT.¹²⁴ Ionic liquid and Lewis acid were also used as solvent and catalyst to attach alkyl groups onto BNNT surface based on $\text{S}_{\text{N}}2$ substitution reaction.¹²⁵ These modification methods can be used to produce well-dispersed BNNT nanocomposite. It's easy to notice that the concentration of edge

Fig. 11 Hierarchy structures. (a) SEM image of cross-sectional view of aligned CNTs grown on a single carbon fiber; (b) SEM image of CNT grown on carbon fiber bundle (Adapted with permission from ref. ¹³¹ Copyright (2013) American Chemical Society); (c) Carbon nanotube fuzzy fiber developed at UDRI; ¹³⁰ (d) CNT grown on graphene; (e) BNNT grown on BN nanosheet; ¹³⁹ (f) C₆₀ encapsulated in CNT ¹³⁸ (Adapted with permission from Nature Springer).

N-H group is relatively low. Thus, for an efficient functionalization, the surface of BNNT has to be broken. One method to introduce extra N-H group is using high energy beam to shoot the BNNT. For example, ammonia plasma can introduce N-H group on the surface of BNNT effectively.^{126, 127} Besides N-H group, B-OH and B-N group are also attacking points. However, due to the stability of the -backbonding, B-N and B-O bonds are hard to be attacked. The functionalization through breaking B-N or B-O bonds is still unexplored. The functionalization on BNNT also changes its electronic structure. It's very interesting that all kinds of functionalization reduce the band gap of BNNT, for example, from 5.80 eV of neat BNNT to 4.20 eV of C₁₀H₂CO-BNNT.¹²⁸ Boron carbonitride (BCN) nanotube can be considered as a kind of carbon doped BNNT as well. It is found that with the addition of carbon atoms, the band gap of BCN material decreases.¹²⁹

4. Hierarchical structures

Nanotubes are relatively simple compared to the state of material science art.¹²² Performance of nanotube-only material is also always not satisfactory. For example, the electromagnetic interference (EMI) shielding range of CNT is relatively low.¹²² A wide band or selected band EMI shielding are required when designing a high performance or multifunctional EMI application. The hierarchical structure is the best solution.

Hierarchical structure means a multi-level and organized structure. Many hierarchical structures are also factual, such as dendritic, branched and layered which usually forms low-density structure either by growth or self-assembly. For example, fuzzy fiber^{130, 131} (Fig. 11a, 11b, 11c) can be produced by growing carbon nanotube on glass fiber or carbon fiber surface and the substrate fiber can be bundled into larger filament.¹³² This 3 levels structure has been used for multifunctional applications.¹³³

However, it's not necessary to be fractal (Fig. 11d, 11e, 11f). A CNT/graphene structure was synthesized for electrochemical and capacitive energy storage application.^{134, 135} Mickelson¹³⁶ and Guan¹³⁷ packed C₆₀ into BNNT/CNT and created one-dimensional crystal of C₆₀ (Fig. 11f).¹³⁸

Nowadays, commercial materials are designed on the molecular level. Besides the choice of elements, structural design affects products' properties significantly. The primary way to control structure is the synthesis method. As shown in table 1, different synthesis methods are evaluated. As a result, CVD and template method are the best choices for designing a complex structure. For example, stealth vehicles are requiring broadband absorption or transparent material. One stealth material only provides narrow band absorption property. However, the compatibility between different materials becomes a problem when using different kinds of materials, such as carbon nanomaterial, metallic nanoparticle and ferrite. As a result, a good solution is to use coupled various carbon nanomaterials. For example, Fe/Co coated carbon fiber provides considerable electromagnetic absorption in the 1-10 GHz region.¹⁴⁰ CNT nanocomposites have excellent electromagnetic shielding in UHF (ballistic missile early warning) and X (marine and airport) radar band.¹⁴¹ Thus, it's predictable that a combination of carbon fiber and CNT has a broader electromagnetic shielding range.¹⁴² On the other hand, multifunctional composite was developed for structural health monitoring applications by growing CNT on carbon fiber.^{130, 133} Of course, besides electromagnetic shielding applications, nanotube-based hierarchical structure can be used in many fields such as catalyst, scaffold, flexible electronics, super-capacitors, etc.

Although the cheapest way to combine different materials is mixing, however, grow them in one piece is the most efficient way. Once the materials are grown into one piece, electron, phonon, and load can be transferred in a more effective way. In summary, the hierarchical

Table 1 Evaluation of different nanotube synthesis methods.

Synthesis methods	Uniformity	Designability (structural)	Reproducibility	Productivity	Price
Arc discharge	poor	poor	good	good	low
Laser ablation	poor	poor	good	good	
Plasma torch	good	fair	good	good	low
CVD	good	good	good	good	fair
Electrochemical method	poor	poor	good	poor	high
Template method	excellent	excellent	good	poor	high
Hydrothermal method	poor	poor	fair	good	fair
Mechanical method	poor	poor	good	good	low

structure is an important and emerging approach in many fields. The common geometrical characteristics for nanotubes are their high surface area, high aspect ratio, and small diameter. When being designed into hierarchical structures, nanotubes' advantages can be enhanced exponentially.

5. Summary

Material science plays a critical role in science/technology and the daily life, such as light emitting devices, smart windows, solar cells and so on.¹⁴³⁻¹⁵³ As a rising star in material science, nanomaterials in form of nanoparticle,^{150,154} nanofiber/wire,¹⁵⁵⁻¹⁵⁸ nanocomposite^{159, 160} have been widely used in many areas.¹⁶¹⁻¹⁶⁶ Nanotubes are one of the most interesting nanomaterials due to their special tubular structure. Fabrication of CNT, BNNT like materials are becoming available in many laboratories. While the grown nanotubes have a high crystallinity, the etched nanotubes are more uniform. Additionally, new nanotubes such as stanene nanotube may come out with astonishing properties since two-dimensional stanene was already made. Despite of material aspects, the design of structure is equally important for the performance of nanomaterial. Hierarchical structures based on nanotubes can response in different levels or different energy regions. For example, the hierarchical carbon nanostructure might be the easiest way to achieve a super black body and wide range electromagnetic wave absorber. As a conclusion, coupling of two materials is not to simply synthesize/mix them together, but also to design a proper structure from the aspect of basic physics and chemistry. Such as designs of electronic structure, crystal plane orientation, nanotube aggregation in confined space, hierarchical structure and charge transfer mechanism. Definitely, the nanotubes are always excellent choices.

Acknowledgement

This work is funded in part by the U. S. Department of Education, Office of Postsecondary Education, Institutional Services (Title III, Part B, HBCU Program)

Conflict of interest

There are no conflicts to declare.

References

1. S. Iijima, *Nature*, 1991, **354**, 56-58.

- Y. B. Yan, J. W. Miao, Z. H. Yang, F. X. Xiao, H. B. Yang, B. Liu and Y. H. Yang, *Chem. Soc. Rev.*, 2015, **44**, 3295-3346.
- S. Wei, X. P. Fu, W. W. Wang, Z. Jin, Q. S. Song and C. J. Jia, *J. Phys. Chem. C*, 2018, **122**, 4928-4936.
- J. T. Grant, C. A. Carrero, F. Goeltl, J. Venegas, P. Mueller, S. P. Burt, S. E. Specht, W. P. McDermott, A. Chieragato and I. Hermans, *Science*, 2016, **354**, 1570-1573.
- M. Aguilar-Romero, R. Camposeco, S. Castillo, J. Marin, V. Rodriguez-Gonzalez, L. A. Garcia-Serrano and I. Mejia-Centeno, *Fuel*, 2017, **198**, 123-133.
- C. Liu, F. Li, L. P. Ma and H. M. Cheng, *Adv. Mater.*, 2010, **22**, 28-62.
- K. Mylvaganam and L. C. Zhang, *Appl. Phys. Lett.*, 2006, **89**, 123127.
- D. Deng, M. G. Kim, J. Y. Lee and J. Cho, *Energ Environ. Sci.*, 2009, **2**, 818-837.
- K. Y. Xie, J. Li, Y. Q. Lai, W. Lu, Z. A. Zhang, Y. X. Liu, L. M. Zhou and H. T. Huang, *Electrochem Commun.*, 2011, **13**, 657-660.
- L. M. Sun, X. H. Wang, Y. R. Wang and Q. Zhang, *Carbon*, 2017, **122**, 462-474.
- C. Liu, I. Sergeichev, I. Akhatov and K. Lafdi, *Compos. Sci. Technol.*, 2018, **159**, 111-118.
- C. Liu and K. Lafdi, *CAMX 2018 – The Composites and Advanced Materials Expo*, Dallas, TX, 2018, TP18-0586.
- H. C. Wu, X. L. Chang, L. Liu, F. Zhao and Y. L. Zhao, *J. Mater. Chem.*, 2010, **20**, 1036-1052.
- T. J. Whitney, T. Gibson, K. Lafdi and B. Welk, *International Mechanical Engineering Congress and Exposition*, 2012, **3**, Pts a-C: Design, Materials, and Manufacturing, 2013, 929-932.
- A. A. Shvedova, A. A. Kapralov, W. H. Feng, E. R. Kisin, A. R. Murray, R. Mercer, C. M. St Croix, M. A. Lang, S. C. Watkins, N. V. Konduru, B. L. Allen, J. Conroy, G. P. Kotchey, B. M. Mohamed, A. D. Meade, Y. Volkov, A. Star, B. Fadeel and V. E. Kagan, *Plos One*, 2012, **7**, 0030923.
- A. M. Wen, M. Infusino, A. De Luca, D. L. Kernan, A. E. Czapar, G. Strangi and N. F. Steinmetz, *Bioconjugate Chem.*, 2015, **26**, 51-62.
- Y. Yamamoto, T. Fukushima, Y. Suna, N. Ishii, A. Saeki, S. Seki, S. Tagawa, M. Taniguchi, T. Kawai and T. Aida, *Science*, 2006, **314**, 1761-1764.
- Z. D. Han and A. Fina, *Prog. Polym. Sci.*, 2011, **36**, 914-944.
- Y. X. Lin, Y. T. Jia, G. Alva and G. Y. Fang, *Renew. Sust. Energ. Rev.*, 2018, **82**, 2730-2742.
- Z. Han and A. Fina, *Prog. Polym. Sci.*, 2011, **36**, 914-944.
- M. Zheng, *Topics Curr. Chem.*, 2017, **375**, 13.
- H. W. Lee, Y. Yoon, S. Park, J. H. Oh, S. Hong, L. S. Liyanage, H. L. Wang, S. Morishita, N. Patil, Y. J. Park, J. J. Park, A. Spakowitz, G. Galli, F. Gygi, P. H. S. Wong, J. B. H. Tok, J. M. Kim and Z. A. Bao, *Nat. Commun.*, 2011, **2**, 541.
- E. A. Laird, F. Kuemmeth, G. A. Steele, K. Grove-Rasmussen, J. Nygard, K. Flensberg and L. P. Kouwenhoven, *Rev. Mod. Phys.*, 2015, **87**, 703-764.

24. T. W. Ebbesen, H. J. Lezec, H. Hiura, J. W. Bennett, H. F. Ghaemi and T. Thio, *Nature*, 1996, **382**, 54-56.
25. L. C. Qin, X. L. Zhao, K. Hirahara, Y. Miyamoto, Y. Ando and S. Iijima, *Nature*, 2000, **408**, 50-50.
26. C. Qin and L. M. Peng, *Phys. Rev. B*, 2002, **65**, 155431.
27. J. H. Warner, N. P. Young, A. I. Kirkland and G. A. D. Briggs, *Nat. Mater.*, 2011, **10**, 958-962.
28. T. D. Yuzvinsky, W. Mickelson, S. Aloni, S. L. Konsek, A. M. Fennimore, G. E. Begtrup, A. Kis, B. C. Regan and A. Zettl, *Appl. Phys. Lett.*, 2005, **87**, 083103.
29. C. Shen, A. H. Brozena and Y. H. Wang, *Nanoscale*, 2011, **3**, 503-518.
30. J. Xiao, M. Q. Long, X. M. Li, H. Xu, H. Huang and Y. L. Gao, *Sci. Rep.-UK*, 2014, **4**, 4327.
31. V. Sresht, A. A. H. Padua and D. Blankschtein, *ACS Nano*, 2015, **9**, 8255-8268.
32. J. Shi, K. Cai, L. N. Liu and Q. H. Qin, *Sci. Rep.-UK*, 2017, **7**, 12951.
33. W. Jiang, X. X. Li, A. B. Guo, H. Y. Guan, Z. Wang and K. Wang, *J. Magn. Magn. Mater.*, 2014, **355**, 309-318.
34. J. L. C. Fajin, M. N. D. S. Cordeiro and J. R. B. Gomes, *Phys. Chem. Chem. Phys.*, 2017, **19**, 19188-19195.
35. J. K. Chen, W. T. Chen, C. C. Cheng, C. C. Yu and J. P. Chu, *Mater. Today*, 2018, **21**, 178-185.
36. L. Guadagno, M. Raimondo, V. Vittoria, L. Vertuccio, K. Lafdi, B. De Vivo, P. Lamberti, G. Spinelli and V. Tucci, *Nanotechnology*, 2013, **24**, 305704.
37. A. C. Yilmaz, M. S. Ozen, E. Sancak, R. Erdem, O. Erdem and N. Soin, *J. Compos. Mater.*, 2018, **52**, 1423-1432.
38. S. Hong and S. Myung, *Nat. Nanotechnol.*, 2007, **2**, 207-208.
39. E. Pop, D. Mann, Q. Wang, K. E. Goodson and H. J. Dai, *Nano Lett.*, 2006, **6**, 96-100.
40. R. Arenal, M.-S. Wang, Z. Xu, A. Loiseau and D. Golberg, *Nanotechnology*, 2011, **22**, 265704.
41. A. Thess, R. Lee, P. Nikolaev, H. J. Dai, P. Petit, J. Robert, C. H. Xu, Y. H. Lee, S. G. Kim, A. G. Rinzler, D. T. Colbert, G. E. Scuseria, D. Tomanek, J. E. Fischer and R. E. Smalley, *Science*, 1996, **273**, 483-487.
42. P. Castrucci, M. Scarselli, M. De Crescenzi, M. Diociaiuti, P. S. Chaudhari, C. Balasubramanian, T. M. Bhave and S. V. Bhoraskar, *Thin Solid Films*, 2006, **508**, 226-230.
43. S. Yamada and H. Fujiki, *Jpn. J. Appl. Phys.*, 2006, **45**, L837-L839.
44. A. Fathalizadeh, T. Pham, W. Mickelson and A. Zettl, *Nano Lett.*, 2014, **14**, 4881-4886.
45. K. S. Kim, C. T. Kingston, A. Hrdina, M. B. Jakubinek, J. W. Guan, M. Plunkett and B. Simard, *ACS Nano*, 2014, **8**, 6211-6220.
46. O. Smiljanic, B. L. Stansfield, J. P. Dodelet, A. Serventi and S. Desilets, *Chem. Phys. Lett.*, 2002, **356**, 189-193.
47. K. S. Kim, G. Cota-Sanchez, C. T. Kingston, M. Imbris, B. Simard and G. Soucy, *J. Phys. D Appl. Phys.*, 2007, **40**, 2375-2387.
48. M. Hikita, R. L. Bradford and K. Lafdi, *Crystals*, 2014, **4**, 466-489.
49. A. N. Obraztsov, *Nat. Nanotechnol.*, 2009, **4**, 212-213.
50. J. E. Butler and A. V. Sumant, *Chem. Vapor Depos.*, 2008, **14**, 145-160.
51. K. E. Kim, K. J. Kim, W. S. Jung, S. Y. Bae, J. Park, J. Choi and J. Choo, *Chem. Phys. Lett.*, 2005, **401**, 459-464.
52. K. Kuwana and K. Saito, *P. Combust. Inst.*, 2007, **31**, 1857-1864.
53. K. Kuwana and K. Saito, *Carbon*, 2005, **43**, 2088-2095.
54. K. Hata, D. N. Futaba, K. Mizuno, T. Namai, M. Yumura and S. Iijima, *Science*, 2004, **306**, 1362-1364.
55. D. N. Futaba, K. Hata, T. Yamada, K. Mizuno, M. Yumura and S. Iijima, *Phys. Rev. Lett.*, 2005, **95**, 056104.
56. R. F. Zhang, Y. Y. Zhang, Q. Zhang, H. H. Xie, W. Z. Qian and F. Wei, *ACS Nano*, 2013, **7**, 6156-6161.
57. C. Schunemann, F. Schaffel, A. Bachmatiuk, U. Queitsch, M. Sparing, B. Rellinghaus, K. Lafdi, L. Schultz, B. Buchner and M. H. Rummeli, *ACS Nano*, 2011, **5**, 8928-8934.
58. A. M. Cassell, J. A. Raymakers, J. Kong and H. J. Dai, *J. Phys. Chem. B*, 1999, **103**, 6484-6492.
59. M. Su, B. Zheng and J. Liu, *Chem. Phys. Lett.*, 2000, **322**, 321-326.
60. B. L. Liu, W. C. Ren, C. Liu, C. H. Sun, L. B. Gao, S. S. Li, C. B. Jiang and H. M. Cheng, *ACS Nano*, 2009, **3**, 3421-3430.
61. B. L. Liu, W. C. Ren, L. B. Gao, S. S. Li, S. F. Pei, C. Liu, C. B. Jiang and H. M. Cheng, *J. Am. Chem. Soc.*, 2009, **131**, 2082-2083.
62. D. Takagi, Y. Kobayashi and Y. Hommam, *J. Am. Chem. Soc.*, 2009, **131**, 6922-6923.
63. D. Sarangi, C. Godon, A. Granier, A. Goullet, G. Turban and O. Chauvet, *Chem. Phys. Lett.*, 2004, **397**, 516-519.
64. M. H. Rummeli, E. Borowiak-Palen, T. Gemming, T. Pichler, M. Knupfer, M. Kalbac, L. Dunsch, O. Jost, S. R. P. Silva, W. Pompe and B. Buchner, *Nano Lett.*, 2005, **5**, 1209-1215.
65. S. Han, X. L. Liu and C. W. Zhou, *J. Am. Chem. Soc.*, 2005, **127**, 5294-5295.
66. M. H. Rummeli, F. Schaffel, C. Kramberger, T. Gemming, A. Bachmatiuk, R. J. Kalenczuk, B. Rellinghaus, B. Buechner and T. Pichler, *J. Am. Chem. Soc.*, 2007, **129**, 15772-15773.
67. L. Szymanski, Z. Kolacinski, S. Wiak, G. Raniszewski and L. Pietrzak, *Nanomaterials-Basel*, 2017, **7**, 45.
68. C. C. Yap, C. Brun, D. L. Tan, H. Li, E. H. T. Teo, D. Baillargeat and B. K. Tay, *Nanoscale Res. Lett.*, 2012, **7**, 1-8.
69. M. Kumar and Y. Ando, *J. Nanosci. Nanotechnol.*, 2010, **10**, 3739-3758.
70. M. Kumar, X. L. Zhao, Y. Ando, S. Iijima, M. Sharon and K. Hirahara, *Mol. Cryst. Liq. Cryst.*, 2002, **387**, 341-345.
71. P. Nikolaev, M. J. Bronikowski, R. K. Bradley, F. Rohmund, D. T. Colbert, K. A. Smith and R. E. Smalley, *Chem. Phys. Lett.*, 1999, **313**, 91-97.
72. M. J. Bronikowski, P. A. Willis, D. T. Colbert, K. A. Smith and R. E. Smalley, *J. Vac. Sci. Technol. A*, 2001, **19**, 1800-1805.
73. H. J. Jeong, S. Y. Jeong, Y. M. Shin, J. H. Han, S. C. Lim, S. J. Eum, C. W. Yang, N. G. Kim, C. Y. Park and Y. H. Lee, *Chem. Phys. Lett.*, 2002, **361**, 189-195.
74. C. Y. Su, W. Y. Chu, Z. Y. Juang, K. F. Chen, B. M. Cheng, F. R. Chen, K. C. Leou and C. H. Tsai, *J. Phys. Chem. C*, 2009, **113**, 14732-14738.
75. I. Gerber, M. Oubenali, R. Bacsa, J. Durand, A. Goncalves, M. F. R. Pereira, F. Jolibois, L. Perrin, R. Poteau and P. Serp, *Chem-Eur J.*, 2011, **17**, 11467-11477.
76. A. R. Kamali and D. J. Fray, *Carbon*, 2014, **77**, 835-845.
77. A. R. Kamali, J. Feighan and D. J. Fray, *Faraday Discuss*, 2016, **190**, 451-470.
78. S. E. R. Geng, Z. Zhu, L. Xie, W. Lu, C. Li and Y. Yao, *Ceramics Internat.*, 2011, **44**, 22794-22799.
79. D. P. Yu, X. S. Sun, C. S. Lee, I. Bello, S. T. Lee, H. D. Gu, K. M. Leung, G. W. Zhou, Z. F. Dong and Z. Zhang, *Appl. Phys. Lett.*, 1998, **72**, 1966-1968.
80. C. H. Lee, S. Bhandari, B. Tiwari, N. Yapici, D. Y. Zhang and Y. K. Yap, *Molecules*, 2016, **21**, 922.
81. A. Rubio, J. L. Corkill and M. L. Cohen, *Phys. Rev. B*, 1994, **49**, 5081-5084.
82. M. W. Smith, K. C. Jordan, C. Park, J. W. Kim, P. T. Lillehei, R. Crooks and J. S. Harrison, *Nanotechnology*, 2009, **20**, 505604.
83. O. R. Lourie, C. R. Jones, B. M. Bartlett, P. C. Gibbons, R. S. Ruoff and W. E. Buhro, *Chem. Mater.*, 2000, **12**, 1808-1810.
84. C. Tang, Y. Bando, T. Sato and K. Kurashima, *Chem. Commun.*, 2002, 1290-1291.
85. Y. Huang, J. Lin, C. C. Tang, Y. Bando, C. Y. Zhi, T. Y. Zhai, B. Dierre, T. Sekiguchi and D. Golberg, *Nanotechnology*, 2011, **22**, 145602.
86. L. Li, X. W. Liu, L. H. Li and Y. Chen, *Microelectron Eng.*, 2013, **110**, 256-259.
87. P. Ahmad, M. U. Khandaker, Z. R. Khan and Y. M. Amin, *RSC Adv.*, 2015, **5**, 35116-35137.
88. Y. Chen, L. T. Chadderton, J. FitzGerald and J. S. Williams, *Appl. Phys. Lett.*, 1999, **74**, 2960-2962.
89. X. D. Li, G. W. Meng, Q. L. Xu, M. G. Kong, X. G. Zhu, Z. Q. Chu and A. P. Li, *Nano Lett.*, 2011, **11**, 1704-1709.
90. H. Wu, G. Chan, J. W. Choi, I. Ryu, Y. Yao, M. T. McDowell, S. W. Lee, A. Jackson, Y. Yang, L. B. Hu and Y. Cui, *Nat. Nanotechnol.*, 2012, **7**, 309-314.
91. C. Z. Wang, X. N. Fu, Y. Y. Guo, Z. X. Guo, C. X. Xia and Y. Jia, *Nanotechnology*, 2017, **28**, 115202.
92. W. K. Hsu, J. P. Hare, M. Terrones, H. W. Kroto, D. R. M. Walton and P. J. F. Harris, *Nature*, 1995, **377**, 687-687.
93. A. T. Dimitrov, G. Z. Chen, I. A. Kinloch and D. J. Fray, *Electrochim Acta*, 2002, **48**, 91-102.
94. A. R. Kamali and D. Fray, *J. Mater. Sci.*, 2016, **51**, 569-576.
95. C. Liu and K. Lafdi, *J. Appl. Polym. Sci.*, 2017, **134**, 45388.
96. Y. Gogotsi, T. Kraft, K. G. Nickel and M. E. Zvanut, *Diam. Relat. Mater.*,

- 1998, **7**, 1459-1465.
97. Y. Gogotsi, J. A. Libera and M. Yoshimura, *J. Mater. Res.*, 2000, **15**, 2591-2594.
 98. C. Velasco-Santos, A. L. Martinez-Hernandez, A. Consultchi, R. Rodriguez and V. M. Castano, *Chem. Phys. Lett.*, 2003, **373**, 272-276.
 99. Y. Chen, J. D. Fitz Gerald, J. S. Williams and S. Bulcock, *Chem. Phys. Lett.*, 1999, **299**, 260-264.
 100. J. Yu, B. C. P. Li, J. Zou and Y. Chen, *J. Mater. Sci.*, 2007, **42**, 4025-4030.
 101. G. X. Zhu, S. M. Dong, J. B. Hu, Y. M. Kan, P. He, L. Gao, X. Y. Zhang and H. J. Zhou, *RSC Adv.*, 2016, **6**, 14112-14119.
 102. Y. Chen, M. J. Conway and J. D. Fitz Gerald, *Appl. Phys. A-Mater.*, 2003, **76**, 633-636.
 103. Santra, H. Y. Ko, Y. W. Yeh, F. Martelli, I. Kaganovich, Y. Raitses and R. Car, *Nanoscale*, 2018, **10**, 22223-22230.
 104. K. Kan, T. L. Xia, L. Li, H. M. Bi, H. F. Fu and K. Y. Shi, *Nanotechnology*, 2009, **20**, 185502.
 105. Y. L. Cheng, B. B. Xia, C. Q. Fang and L. Yang, *J. Mater. Sci. Technol.*, 2017, **33**, 1187-1194.
 106. K. F. Fu, W. J. Huang, Y. Lin, L. A. Riddle, D. L. Carroll and Y. P. Sun, *Nano Lett.*, 2001, **1**, 439-441.
 107. Y. P. Sun, W. J. Huang, Y. Lin, K. F. Fu, A. Kitaygorodskiy, L. A. Riddle, Y. J. Yu and D. L. Carroll, *Chem. Mater.*, 2001, **13**, 2864-2869.
 108. Y. D. Yang, L. T. Qu, L. M. Dai, T. S. Kang and M. Durstock, *Adv. Mater.*, 2007, **19**, 1239-1243.
 109. J. K. Lim, W. S. Yun, M. H. Yoon, S. K. Lee, C. H. Kim, K. Kim and S. K. Kim, *Synthetic Met.*, 2003, **139**, 521-527.
 110. N. O. V. Plank, R. Cheung and R. J. Andrews, *Appl. Phys. Lett.*, 2004, **85**, 3229-3231.
 111. D. Janas, S. Boncel and K. K. K. Koziol, *Carbon*, 2014, **73**, 259-266.
 112. Z. S. Qian, J. J. Ma, J. Zhou, P. Lin, C. C. Chen, J. R. Chen and H. Feng, *J. Mater. Chem.*, 2012, **22**, 22113-22119.
 113. V. Datsyuk, M. Kalyva, K. Papagelis, J. Parthenios, D. Tasis, A. Siokou, I. Kallitsis and C. Galiotis, *Carbon*, 2008, **46**, 833-840.
 114. Y. P. Sun, K. F. Fu, Y. Lin and W. J. Huang, *Accounts Chem. Res.*, 2002, **35**, 1096-1104.
 115. Y. Kanai, V. R. Khalap, P. G. Collins and J. C. Grossman, *Phys. Rev. Lett.*, 2010, **104**, 066401.
 116. K. M. Lee, L. C. Li and L. M. Dai, *J. Am. Chem. Soc.*, 2005, **127**, 4122-4123.
 117. L. T. Qu and L. M. Dai, *Chem. Commun.*, 2007, 3859-3861.
 118. L. T. Qu, L. M. Dai and E. Osawa, *J. Am. Chem. Soc.*, 2006, **128**, 5523-5532.
 119. M. H. Miao, S. C. Hawkins, J. Y. Cai, T. R. Gengenbach, R. Knott and C. P. Huynh, *Carbon*, 2011, **49**, 4940-4947.
 120. J. X. Guo, Y. G. Li, S. W. Wu and W. X. Li, *Nanotechnology*, 2005, **16**, 2385-2388.
 121. M. C. Evora, D. Klosterman, K. Lafdi, L. Li and J. L. Abot, *Carbon*, 2010, **48**, 2037-2046.
 122. N. Li, Y. Huang, F. Du, X. B. He, X. Lin, H. J. Gao, Y. F. Ma, F. F. Li, Y. S. Chen and P. C. Eklund, *Nano Lett.*, 2006, **6**, 1141-1145.
 123. C. Y. Zhi, Y. Bando, C. C. Tang, S. Honda, K. Sato, H. Kuwahara and D. Golberg, *Angew. Chem. Int. Edit.*, 2005, **44**, 7932-7935.
 124. C. Y. Zhi, Y. Bando, C. C. Tang, H. Kuwahara and D. Golberg, *J. Phys. Chem. C*, 2007, **111**, 1230-1233.
 125. C. Y. Zhi, Y. Bando, W. L. Wang, C. C. Tang, H. Kuwahara and D. Golberg, *J. Phys. Chem. C*, 2007, **111**, 18545-18549.
 126. T. Ikuno, T. Sainsbury, D. Okawa, J. M. J. Frechet and A. Zettl, *Solid State Commun.*, 2007, **142**, 643-646.
 127. T. Sainsbury, T. Ikuno, D. Okawa, D. Pacile, J. M. J. Frechet and A. Zettl, *J. Phys. Chem. C*, 2007, **111**, 12992-12999.
 128. C. Y. Zhi, Y. Bando, C. C. Tang and D. Golberg, *Phys. Rev. B*, 2006, **74**, 153413.
 129. C. Y. Zhi, J. D. Guo, X. D. Bai and E. G. Wang, *J. Appl. Phys.*, 2002, **91**, 5325-5333.
 130. M. Bouchard, K. Lafdi, N. Schehl, J. Sebastian and Y. Yoon, Ed. U. S. A. Force, Defense Technical Information Center, Wright-Patterson Air Force Base, 2010, FRL-RX-WP-TR-2011-4122.
 131. S. A. Steiner, R. Li and B. L. Wardle, *ACS Appl. Mater. Inter.*, 2013, **5**, 4892-4903.
 132. Q. H. Zhang, J. W. Liu, R. Sager, L. M. Dai and J. Baur, *Compos. Sci. Technol.*, 2009, **69**, 594-601.
 133. M. Boehle, P. Pianca, K. Lafdi and F. Chinesta, *Adv. Aircr. Spacecr. Sci.*, 2015, **2**, 263-273.
 134. L. C. Li and K. Lafdi, *Sensor Actuat B-Chem.*, 2008, **132**, 202-208.
 135. D. S. Yu, K. Goh, H. Wang, L. Wei, W. C. Jiang, Q. Zhang, L. M. Dai and Y. Chen, *Nat. Nanotechnol.*, 2014, **9**, 555-562.
 136. W. Mickelson, S. Aloni, W. Q. Han, J. Cumings and A. Zettl, *Science*, 2003, **300**, 467-469.
 137. L. H. Guan, K. Suenaga, Z. J. Shi, Z. N. Gu and S. Iijima, *Phys. Rev. Lett.*, 2005, **94**, 045502.
 138. B. W. Smith, M. Monthieux and D. E. Luzzi, *Nature*, 1998, **396**, 323-324.
 139. Y. X. Song, B. Li, S. W. Yang, G. Q. Ding, C. R. Zhang and X. M. Xie, *Sci. Rep-UK*, 2015, **5**, 10337.
 140. L. Wang, F. He and Y. Z. Wan, *J. Alloy Compd.*, 2011, **509**, 4726-4730.
 141. A. Kolanowska, D. Janas, A. P. Herman, R. G. Jedrysiak, T. Gizewski and S. Boncel, *Carbon*, 2018, **126**, 31-52.
 142. M. G. Jang, S. C. Ryu, K. J. Juhn, S. K. Kim and W. N. Kim, *J. Appl. Polym. Sci.*, 2018, 47302.
 143. X. Tu, X. Fu and Q. Jiang, *Displays*, 2010, **31**, 150-154.
 144. Y. F. Gong, X. K. Fu, S. P. Zhang and Q. Jiang, *Chin. J. Chem.*, 2007, **25**, 1743-1747.
 145. Q. Jiang, M. Chen, J. Li, Y. Xin, X. Shan, B. Pan, C. Wang, S. Lin, T. Siegrist, Q. Xiao and Z. Yu, *ACS Nano*, 2017, **11**, 1073-1079.
 146. Q. Jiang, X. Zeng, N. Wang, Z.-L. Xiao, Z. Guo and J. Lu, *ACS Energy Lett.*, 2018, **3**, 264-269.
 147. Q. Jiang, L. Wang, C. Yan, C. Liu and Z. Guo, *Eng. Sci.*, 2018, **1**, 64-68.
 148. Q. Jiang and T. Xu, *Comments Inorg. Chem.*, 2015, **36**, 200-214.
 149. J. Zhao, L. Wu, C. Zhang, B. Zeng, Y. Lv, Z. Li, Q. Jiang and Z. Guo, *J. Mater. Chem. C*, 2017, **5**, 3903-3907.
 150. Q. Jiang, Y. Yeh, N. Lu, H. Kuo, M. Lesslie and Tao Xu, *J. Renew. Sustain. Ener.*, 2016, **8**, 013701.
 151. Y. Wang, J. Li, J. Li, C. Duan, H. Zhang, H. Jian, L. He, G. Tao, C. Yan and T. Jiu, *Solar Energy*, 2018, **160**, 353-359.
 152. Y. Wang, C. Duan, J. Li, W. Han, M. Zhao, L. Yao, Y. Wang, C. Yan and T. Jiu, *ACS Appl. Mater. Inter.*, 2018, **10**, 20128-20135.
 153. Q. Du, Y. Zhou, X. Pan, J. Zhang, Q. Zhuo, S. Chen, G. Chen, T. Liu, F. Xu and C. Yan, *RSC Advances*, 2016, **6**, 54589-54596.
 154. Q. Jiang, F. Liu, T. Li and T. Xu, *J. Mater. Chem. C*, 2014, **2**, 618-621.
 155. E. Ghafari, X. Jiang and N. Lu, *Adv. Compos. Hybr. Mater.*, 2018, **1**, 332-340.
 156. Y. Ma, M. Ma, X. Yin, Q. N. Lu, Yi, Y. Lu, E. Wujcik, X. Mai, C. Wang and Z. Guo, *Polymer*, 2018, **156**, 128-135.
 157. E. Ghafari and N. Lu, *Compos. B Eng.*, 2018, **160**, 1-9.
 158. Q. Jiang, X. Sheng, Y. Li, X. Feng and T. Xu, *Chem. Commun.* 2014, **50**, 14720-14723.
 159. E. Wujcik, L. Lyu, J. Liu, H. Liu, C. Liu, Y. Lu, K. Sun, R. Fan, N. Wang, N. Lu and Z. Guo, *Eng. Sci.*, 2018, **2**, 26-42.
 160. M. Idrees, S. Batool, J. Kong, Q. Zhuang, H. Liu, Q. Shao, N. Lu, Y. Feng, E. Wujcik, Q. Gao, T. Ding, R. Wei and Z. Guo, *Electrochim. Acta*, 2019, **296**, 925-937.
 161. Y. Guo, T. Liu, N. Wang, Q. Luo, H. Lin, J. Li, Q. Jiang, L. Wu and Z. Guo, *Nano Energy*, 2017, **38**, 193-200.
 162. F.-Q. Liu, G.-H. Li, S.-W. Luo, W. Li, Z.-G. Huang, W. Li, F. Su, C.-Q. Li, Z.-B. Ding and Q. Jiang, *ACS Appl. Mater. Interfaces*, 2019, **11**, 1, 691-698.
 163. J. Zhao, L. Wu, C. Zhang, T. Li, Q. Jiang, F. Wang, P. Zhao, J. Ryu and Z. Guo, *Mater. Res. Bull.*, 2018, 19-24.
 164. Q. Jiang, X. Zeng, L. Ge, X. Luo and L. He, *Multifunctional Nanocomposites for Energy and Environmental*, 2018, John Wiley Publisher.
 165. T. Tong, D. Fu, A. X. Levander, W. J. Schaff, B. N. Pantha, N. Lu, B. Liu, I. Ferguson, R. Zhang, J. Y. Lin, H. X. Jiang, J. Wu and D. G. Cahill, *Appl. Phys. Lett.*, 2013, **102**, 121906.
 166. Q. Hao, D. Xu, N. Lu and H. Zhao, *Phys. Rev. B*, 2016, **93**, 205206.