Review Article

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Recent progress in the synthesis and applications of vertically aligned carbon nanotube materials

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Abstract: Vertically aligned carbon nanotube (VACNT) materials is a promising candidate in different fields. The intrinsic performance of VACNTs, such as a large specific surface area, high conductivity, and especially its vertical conductive channel, stands out the VACNTbased device from conventional carbon material-based devices in the energy, environmental sustainability, and so on. In this review, a comprehensive and in-depth summary on the synthesis method and fundamental mechanisms, and design strategies for the novel VACNT materials, is presented. In addition, an overview of the latest development in high-efficiency utilization of VACNT materials in representative fields, including energy storage and conversion, catalysis, terahertz spectroscopy, biology and biomedicine, and environmental sustainability, is given. Finally, the challenges and promising perspectives of VACNT materials in future development are outlined.

Keywords: vertically aligned carbon nanotubes, high orientation, mechanism, energy, environmental sustainability

1 Introduction

Carbon nanotubes (CNTs) can be viewed as tubular structures made of curled graphene sheets. The average diameter of CNTs is about a few to several tens of nanometers, and under certain conditions it can even reach the micron level [1]. In

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addition, CNTs possess various excellent properties including good electric conductivity, splendid modulus of elasticity (~1 TPa), and outstanding chemical stability [2]. However, there have been several problems, such as the poor interaction between CNTs and current collector, the low specific surface area (SSA), which hinder the application in the different fields. To reduce the influence of these undesirable factors, researchers mainly adopted self-assembly method to prepare relatively vertically aligned CNTs (VACNTs). In addition to the inherent properties of carbon materials, VACNTs possess unique performance, such as high surface area, good electrical conductivity, large aspect ratios, and high orientation. Therefore, in recent years, VACNTs have been widely used in different fields, including supercapacitors (SCs), rechargeable batteries, energy conversion devices (solar cells), terahertz (THz) technologies (polarizers, generators, and detectors), and electron emitters [3]. As shown in Figure 1, the excellent performance of VACNTs and their applications in different fields are summarized.

In this review, we focus on the recent progress on the VACNTs and their composites. The synthesis methods and mechanism were discussed and highlighted. Since the structure and morphology of the VACNTs play a critical role in its application in different fields, an important part of this review will focus on their synthesis mechanism. Moreover, we discuss the applications of VACNTs for energy storage and conversion, THz, and environmental sustainability. Differing from the application of VACNTs in a single field, this review summarizes the applications and roles of VACNTs in various fields, thus giving the reader a new understanding of VACNTs. Finally, the main challenges, promising directions and potential application of VACNT are proposed to motivate next-generation VACNT-based novel device.

2 Synthesis of VACNTs

To realize the efficient use of VACNTs in different fields, it is of great significance to research the synthesis method

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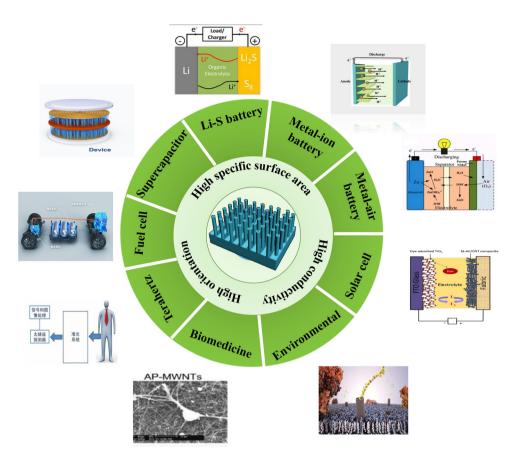


Figure 1: An overview of VACNT-based materials with excellent performance for advanced devices and their potential application in different fields. The insertion diagram in the middle is a VACNTs array. Copyright 2014, American Chemical Society.

and mechanism of VACNTs. At present, there are mainly two CNTs preparation methods: (1) physical and (2) chemical. Accordingly, the growth mechanism of CNTs is also discussed detail in this part.

the mechanism images is shown in Figure 2(b). The preparation of oriented CNTs by physical methods is simple and feasible without strict process control of the growth of

2.1 Synthesis method of VACNTs

2.1.1 Physical method

The physical method can be divided into arc discharge and laser ablation methods [4]. The schematics of the first method are shown in Figure 2(a), and the basic process is as follows: first, two carbon rods electrodes are placed in an inert low-pressure atmosphere; second, the electrons excited from cathode strike the anode when passing a direct current between the two electrodes. Finally, the evaporated carbon is formed as CNTs on the cathode. For the laser ablation method, a laser beam is focused on a carbon target doped with a catalyst in Ar atmosphere. The evaporated catalyst attached to the carbon further promoting the synthesis of VACNTs and

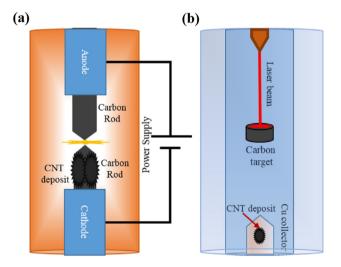


Figure 2: Schematic of (a) arc discharge method and (b) laser ablation method [4]. Copyright 2020, Elsevier.

CNTs, whereas the disadvantages of this method are that the density of CNT arrays is small, the phenomenon of agglomeration often occurs, and most important is required high synthesis temperature (3,000–4,000°C).

2.1.2 Chemical vapor deposition (CVD) method

According to the above description, higher temperature is required to prepare VACNTs using physical methods, which makes the preparation process more complex. Therefore, CVD method, an established technique for the synthesis of high-quality film materials such as silicon, carbides, oxides, and nitrides, has been proposed. At present, the most commonly used CVD methods are thermal CVD (TCVD) and plasma-enhanced CVD (PECVD).

2.1.2.1 TCVD

This method is generally achieved by selecting suitable reactants and catalysts that need to be decomposed at suitable temperatures. The synthesis process is as follows: Two or more gaseous sources are injected into a reaction chamber, and then these sources react with each other at a certain temperature to form a new material which deposits on the substrate. Halonen *et al.* [5] researched the influence of different carbon sources (such as methanol, xylene, and acetylene) and catalysts on the morphology and structure of VACNTs. For the single catalyst, the growth of VACNTs is carried out at 400–600°C

when xylene was used as a carbon source. The VACNTs obtained by this method are short in length and have high defectivity (Figure 3(a and b)). In addition, the system of Fe₂Co-supported Nb₂O₅ as catalyst and acetylene as carbon source was studied [6]. The morphology of the obtained VACNTs is shown in Figure 3(c and d). Compared with using a single catalyst, the use of multiple catalysts is more beneficial to the growth of VACNTs.

2.1.2.2 PECVD

PECVD is mainly used to promote the decomposition of carbon source materials at lower temperatures to obtain VACNTs. Li et al. [7] synthesized dense and aligned VACNTs using Ni/Al/Ni as the catalyst at low temperature and the morphology images are shown in Figure 3(e-h). The Al layer between the two nickel layers fixed the nickel catalyst onto the substrate to form nanoparticles. The growth process of VACNTs in the PECVD system is as follows: First, the samples were annealed in a mixture gas (such as H_2/N_2) at 2.8 Torr. Second, methane is used as a carbon source to grow the VACNTs, and the plasma power and temperature is 200 W and 350°C, respectively [8]. Finally, VACNTs with an average diameter of 20 nm were obtained. In addition, Huang et al. [9] synthesized VACNTs at the low temperature (350–400°C) using H_2/CH_4 as mixture gas at 10 Torr. TEM characterization indicated that the diameter of the prepared VACNTs is approximate 43 nm. Ji et al. [10] demonstrated for the first time that PECVD can grow CNFs at room temperature. The synthesis

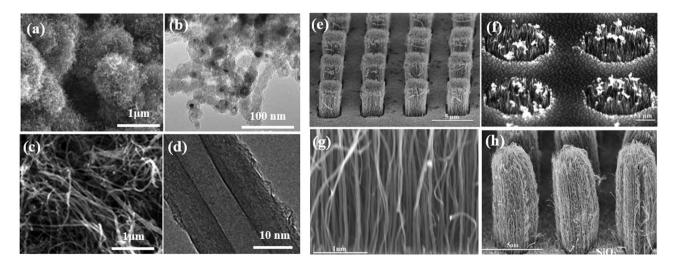


Figure 3: (a) Scanning electro microscopy (SEM) diagram of short CNTs. (b) Transmission electro microscopy (TEM) image of CNTs [5]. Copyright 2011, Wiley. (c) SEM image of CNTs grown on Fe₂Co and (d) the TEM image of a well-structured CNT [6]. Copyright 2010, American Chemical Society. SEM mages of (e) 3 μm CNT *via* selective growth at 420°C, and (f) CNT *via* after O₂ plasma treatment [7]. Copyright 2017, The Royal Society of Chemistry. (g) SEM images of CNT grown on Ti silicide with Ni/Al/Ni multilayer catalyst using PECVD. (h) SEM image of selectively formed CNT array [8]. Copyright 2018, Elsevier.

of CNFs was performed in a PECVD system with a 200 W power and 1,000 mbar pressure. In this process of the synthesis, Ni powder is regarded as catalyst and the CH_4/H_2 as mixture gas. The diameter and the growth rate are approximately 50 nm and 300 nm min⁻¹, respectively.

Despite encouraging results seen in some of the reports, structure defects, length, and growth rate of VACNTs are directly affected by low temperature. Furthermore, the synthesis conditions are relatively strict, the maturity of technology is insufficient, and even the cost is high and unsuitable for large-scale synthesis. Therefore, TCVD method with the advantage of the low-cost and large-scale synthesis has become the preferred method for researchers. In addition, we list the synthesis method of the CNTs and the comparison of different methods. Table 1 is as follows.

2.2 Synthesis mechanism of VACNTs

At present, a generally accepted synthesis mechanism of VACNTs is shown in Figure 4. For the "bottom growth

pattern," the carbon source gas adheres to the surface of the catalyst and decomposes into carbon atoms, which are then dissolved and diffused into the catalyst. When carbon atoms reach supersaturation in the catalyst, they separate out from the top of the catalyst and form VACNTs at the top, while the catalyst particles are attached to the substrate. For the "top growth pattern," the carbon atoms are separated from the junction between the catalyst and the substrate to form the VACNTs structure. Namely, the catalyst particles are lifted up during the growth of VACNTs and sealed by the catalyst particles. In general, VACNTs carry out the "top growth pattern" when the catalyst has a weak interaction with the substrate.

In addition, for TCVD growth of VACNTs, a carbon source gas such as C_2H_2 , CH_4 is introduced into the reaction chamber, and a metal catalyst (Fe, Ni, Co, and so on) is used. If the catalyst is deposited on the substrate in advance, this method is known as the substrate method. In this method, the catalyst is deposited on an appropriate substrate before growth by means of magnetron sputtering or chemical etching. Nevertheless, when the catalyst enters the reaction chamber in the form of an

Table 1: A comparison of the CNT synthesis method

Synthesis method		Synthesis condition	Merit and demerit
Physical method	Arc discharge	Carbon rods	Merit:
		Inert atmosphere	Simple process
		Low press	Demerit:
		Power supply	Ultrahigh temperature
			(3,000-4,000°C)
			Low purity
	Laser ablation	Laser	Merit:
		Catalyst	Simple process
		Ar atmosphere	Demerit:
		Carbon target	Ultrahigh temperature
			(3,000-4,000°C)
			Low purity
CVD	TCVD	Carbon sources	Merit:
		Inert atmosphere	Atmospheric
		Catalyst	Pressure or vacuum
		Substrate	Controllable
			Low cost
			Demerit:
			Low purity
			High temperature
	PECVD	Carbon sources	Merit:
		Inter atmosphere	Low temperature
		Different press	Easy film-forming
		Substrate	Demerit:
			High cost
			Intense radiation
			Strict condition

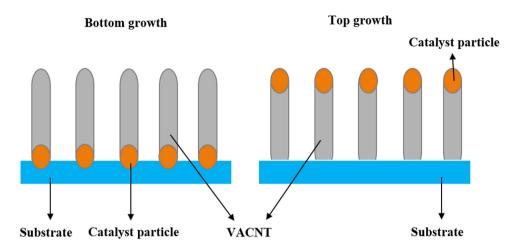


Figure 4: The growth patterns of VACNTs on substrate: bottom growth and top growth.

atmosphere with the carbon source gas, this method is called a floating catalyst [11]. This approach can provide an opportunity for continuous growth, as the carbon source gas and the catalyst can be supplied at the same time. For the methods discussed above, the choice of the growth temperature, catalysts, growth time, and so on are the key parameters that affect the diameter, length, and density of VACNTs [12]. Therefore, the research of synthesis parameters has been discussed in the following paras.

2.2.1 Effect of growth temperature

During the preparation of VACNTs by CVD, both the cracking of the carbon source in the reaction chamber and the structure of the catalyst iron nanoparticles are directly influenced by temperature; that is, the structure and morphology of the VACNTs are very closely related to the growth temperature. Therefore, it is necessary to discuss the effect of growth temperature on VACNTs. According to the relationship between temperature and growth rate [13], the length of VACNT is affected by temperature. When the growth temperature is low, the decomposition of the carbon source is incomplete and the activity of the catalyst is low, which is not conducive to the growth of VACNTs. With the increase of temperature, the degree of catalyst cracking and the activity of carbon atoms are gradually enhanced, which leads to an increase in the growth rate of VACNTs. However, when the temperature continues to increase, the catalyst cleavage is too high and, thus, catalyst particle poisoning occurs [14]. At this moment, the catalyst loses activity and further affects the growth rate of VACNTs.

2.2.2 Effect of catalyst

According to the synthesis mechanism of VACNTs, the choice of catalyst is the key to the preparation of VACNTs. The catalyst plays a crucial role in the morphology and structure of the cracking products as the active center of carbon source decomposition and the center of carbon deposition [15]. The most suitable catalysts are the transition metals, such as Fe, Co, Ni, and so on. Due to the high carbon solubility of these transition metals, certain carbons can be formed, and the carbon atoms have high diffusion rate in these transition metals. The nucleation and growth of VACNTs can be carried out only due to the high diffusion rate of carbon atoms in these transition metals. In addition, two-component or multicomponent metal catalysts can combine the advantages of a single element to achieve optimal results. Therefore, the influence of different types of catalysts offers more options for researchers to improve the growth conditions of VACNTs.

2.2.3 Effect of the carbon sources

All physical forms of carbon sources, namely gas, liquid, and solid, are used for the growth of VACNTs. Carbon source gases can be introduced directly in the reaction chamber, whereas the liquid sources are evaporated in a specific temperature before their admittance in the chamber. Currently, the commonly used carbon source gases are acetylene, ethylene, methane, and so on. In addition, ferrocene, naphthalene, and other organic can be regarded as a liquid carbon source to grow VACNTs by evaporation.

2.2.4 Effect of the growth time

The growth process of VACNTs includes the dissolution, diffusion, and nucleation, and the formation of carbon atom clusters and graphite layers at the later stage of growth. Therefore, it is essential to research the effect of growth time on the VACNTs. When the growth time is short, the growth of VACNTs is in the initial stage. With the increase of time, the distribution density and height of VACNTs gradually increase, and some VACNTs squeeze each other and form carbon tube bundles with certain directionality under the action of van der Waals force. At this point, carbon tubes are in the second stage, that is, the formation of carbon tube bundles. Highly arrayed and uniformly distributed CNTs can be grown with increasing growth time. However, it is not the case that the longer the growth time, the better the array of VACNTs. This can be attributed to the fact that as the time continues to increase, the catalyst particles will gradually deactivate and thus affect the further growth of the VACNTs. Therefore, the growth of VACNTs is superior in a certain period. The specific growth pattern will be studied in a future article.

3 High SSA and excellent conductivity of VACNT for versatile applications

VACNTs with high SSA and large pore size are ideal electrodes for energy-storage devices. On the one hand, VACNTs have adjustable lengths, suitable tube diameters, and large length-to-diameter ratios, which make them very useful in energy-storage field. On the other hand, VACNTs possess excellent mechanical strength and flexibility, which makes them widely used in portable, flexible, wearable electronic products, and electric vehicles [16]. In this part, we first introduce the applications of CNT array as active material in energy storage and energy conversion and then summarize the application of CNT array as a catalytic material in a fuel cell. Finally, the application of CNT array in sensor is discussed.

3.1 As an active material in energy-storage applications

3.1.1 SCs

SCs, a high-power density and long cycle life energy-storage device, can fill the gap between rechargeable batteries and standard capacitors. SCs can be divided into electrical double-layer capacitors and pseudocapacitors according to their energy-storage mechanism. Large SSA and rapid transfer-diffusion of electrolyte ions are the requirements of the SC to achieve high-power density, long cyclic stability, and fast charge–discharge rate. CNTs with their high SSA, excellent electrical performance, suitable pore structure, and remarkable thermal and mechanical stability are ideal electrode materials for SCs. Disordered CNTs have been studied as electrode materials for SCs, especially in high-power devices [17]. Generally, disordered CNTs have a smaller SSA (approximately 500 m 2 g $^{-1}$) and mass specific capacitance (4–150 F g $^{-1}$) [18]. This is mainly caused by the poor utilization of the pore volume in the CNTs electrode.

Therefore, constructing appropriate transport channels of electrons and ions is key in improving the SC performance. VACNTs have not only large SSA to increase the accessibility of electrolytes but also high conductivity to further improve the performance of the devices. Therefore, the nanostructure materials based on VACNTs are promising. Recently, some researches have indicated that VACNTs have more advantages than disorderly entangled CNTs in the application of SCs. First, the structure of VACNTs is more suitable for SCs. Compared with the irregular pore structure of nonarray CNTs, the regular structure and good tube spacing in the VACNT array provide more available surface for the electrolyte. Second, the aligned structure could also improve charge storage/conversion performance, which is because each tube can be connected directly to a common electrode, further enabling them to participate effectively in the chargedischarge process. This phenomenon manifests that all the individual tubes of the VACNT electrode contribute specific capacitance, resulting in the increase in energy density. Conversely, the stored energy can be released quickly through each tube of VACNT electrode, thus showing better power performance. In addition, under specific conditions, the upper end of the VACNT can be opened by plasma etching method [19], and then the electrolyte enters the inside of VACNTs, which further increases the opportunities of contact between the VACNT and the electrolyte ion. Recent studies have also indicated that the electrochemical performance of VACNTs is higher than that of nonarray CNTs. For example, Zhang et al. [20] synthesized a manganese oxide nanoflower/VACNT composite electrodes, and the synthesis process is shown in Figure 5(a). Figure 5(b-e) exhibited the morphology and microstructure of VACNT and the manganese oxide/VACNT composite materials. The electrochemical test results indicated an excellent rate capability (50.8% capacity retention at 77 A g^{-1}), high capacitance (199 F g⁻¹), and long cycle life (3% capacity loss after

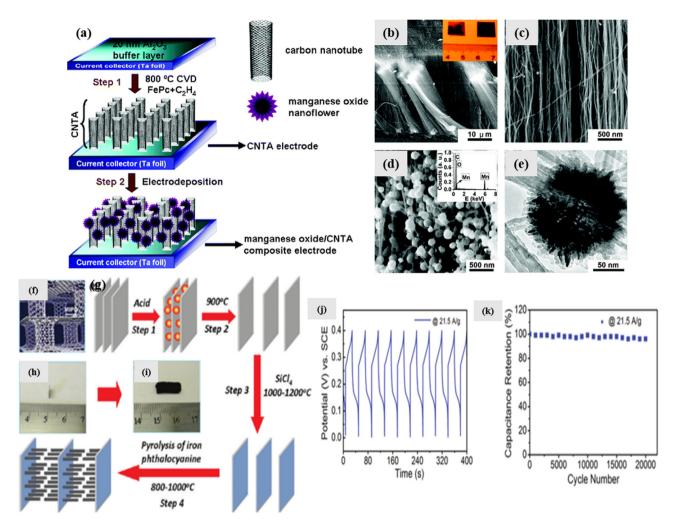


Figure 5: A typical example of VACNT electrode materials for an SC. (a) Preparation process of manganese oxide/VACNT composite materials. The morphology and microstructure of VACNT and the manganese oxide/VACNT composite materials. (b and c) SEM images with different magnifications of the VACNT and a photo (inset of a) of the original (left) and VACNT-covered (right) Ta foil. (d) SEM image of manganese oxide/VACNT composite materials and its EDX pattern (inset). (e) TEM image of a manganese oxide nanoflower [20]. Copyright 2008, American Chemical Society. (f) Schematic of a three-dimensional (3D)-pillared VACNT-graphene nanostructure. (g) Schematic of the procedure for the preparation of the 3D-pillared VACNT-graphene architectures. Photograph of (h) original highly oriented pyrolytic graphite (HOPG) with a thickness of 80 µm and (i) the thermally expanded graphene layers intercalated with VACNTs. (j) The galvanostatic charge-discharge (GCD) curve and (k) cycling stability of the VACNT-based SC [30]. Copyright 2011, American Chemical Society.

20,000 charge—discharge cycles). Compared with nonarray CNT-based SC, the VACNT-based SC can further facilitate an effective energy storage and achieve higher energy density, power density, and outstanding cycling stability.

The SSA of VACNTs needs to be further improved although the performance of VACNTs for SCs is excellent. Researchers found that the large SSA of the materials can also be accomplished by the activation of VACNTs. This method can improve their ability to store electrolyte ions by introducing pores for ion diffusion and adsorption. At present, there are two main activation methods: thermochemical activation and electrochemical activation.

3.1.1.1 Thermochemical activation

This method mainly includes heat treatment and active chemicals [21]. The distribution of pore size and SSA on activated VACNTs was attributed to the type of reactive chemical used, the heating temperature, and time [22]. Figure 6(a and b) shows the SEM images of CNTs before and after thermochemical activation. From Figure 6(a), we can see that the nonactivated CNT possess smooth surface, whereas the resultant activated CNT still retains its original structure after activation. The generation of large numbers of pores by activation can increase

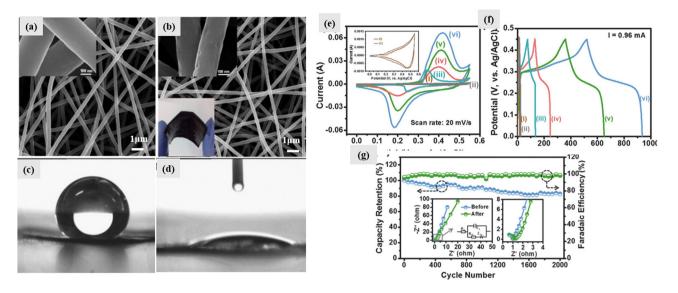


Figure 6: SEM images of (a) electrospun carbon nanotube and (b) ZnCl₂-activated carbon nanotube. The high-magnification images are at the upper left of (a) and (b). A contact angle test in the surface of the nonactivated CNT (c) and active CNT (d) [22]. Copyright 2014, Elsevier. (e) cyclic voltammetry (CV) curves and (f) GCD curves of the treated different CNTs and their composites. (g) Cycling stability of NiO@CNT@CuO [28]. Copyright 2017, Wiley.

the SSA and further improve the specific capacitance. Figure 6(c and d) indicates the contact angle test of the nonactivated and activated CNTs. These results further demonstrate that the activated CNT has better wettability so that ions of the electrolyte are better adsorbed on the electrode surface. Furthermore, the thermal activation of reactive gases such as carbon dioxide and water (steam) is more convenient and environmentally friendly than other liquid or solid chemicals [23].

3.1.1.2 Electrochemical activation

For the electrochemical activation process, the VACNTs is usually used as the anode and oxidized at an appropriate positive potential in the aqueous electrolyte (*e.g.*, HNO₃ [24], Na₂SO₄ [25], H₂SO₄ [26], or pure water [27]). After activation, the specific capacity increased significantly due to the increase of SSA and the formation of oxygen functional groups, which is beneficial to the redox reaction of electrolyte during charge–discharge. Yan and their group [28] demonstrated that a good rate performance and cyclic stability were obtained after electrochemical activation. Electrochemical activation can also improve the mechanical properties of electrode materials through changing potential and electrolyte.

Furthermore, mixing two materials with high SSA can also increase the SSA of the VACNTs electrode material, thus improving the electrochemical performance of

the material. It is well known that VACNTs and graphene have large SSAs and high conductivity, the hybrid network structure of the two materials could act as conductive channels for ions and electrons. Recent researches [29–33] have found that the performance of 3D structure, consisting of VACNT mixed with parallel graphene as electrode material is better than that of nonarray CNT and single array CNT. The 3D-pillared VACNT-graphene structure possesses ideal transport and mechanical properties while maintaining the stability of the structure. Shao et al. [30] used computer models to do research and found that the thermal transport characteristics of the 3D VACNT/graphene structure were controlled by the length of the CNT and the minimum interpillar distance. The 3D VACNT/graphene structures can be used in many fields due to their excellent mechanical and electrical properties, especially advanced SCs. Based on the theoretical models, Shen et al. [31] synthesized a novel 3D VACNT-graphene architecture, and the length of VACNT can be adjusted by changing the preparation parameters. Furthermore, the 3D structure electrode material with high specific capacitance and excellent rate capability greatly exceeds many of the electrode materials currently used in the most advanced SCs. As a flexible SC with a doublelayer structure, novel 3D VACNT-graphene demonstrated high specific energy $70.7 \,\mathrm{W}\,\mathrm{h}\,\mathrm{kg}^{-1}$ at $0.5 \,\mathrm{A}\,\mathrm{g}^{-1}$, and the cycling retention is approximately 97% during chargedischarge of 20,000 cycles. The above results indicate that 3D VACNT hierarchical structures are a promising

electrode material for SCs. Figure 6(e-g) indicates the electrochemical performance of CNTs after electrochemical activation. After 2,000 cycles, the capacity retention and Faradaic efficiency are about 82.72 and 98.2%, respectively, indicating an excellent electrochemical performance. The electrochemical properties of VACNTs and their composites as electrode materials for SCs obtained under different preparation processes are summarized in Table 2.

Furthermore, VACNT/metal oxides and VACNT/conductive polymer offer a new dimension in nanostructure carbonbased energy-storage materials. The role of VACNTs in composites mainly includes the following aspects:

- 1. Outstanding interaction of the VACNTs with the other active materials.
- 2. Formation of open mesoporous network through the array of nanotubes allows fast and efficient migration of the ions to the active surfaces of the composite material.
- 3. VACNTs are highly elastic; thus, the composite electrodes can easily adapt to volume changes during charging and discharging, further improving cycling performance.

For example, Seah et al. [46] synthesized a hematite/ multi-walled carbon nanotubes (MWCNT) composite material as the anode of the energy-storage device and shown a high energy density of 50W h kg⁻¹ at a potential range of 0-2.8 V. The excellent electrochemical performance can be attributed to the microporous structure of the VACNTs providing suitable sites for the deposition of the hematite. In addition, VACNTs provide vertical conductive channels for the migration of electrolyte ions, resulting in shorter migration paths. Zhang et al. [47] studied the cyclic stability of the amorphous MnO₂ and VACNT composite. Compared with the pure MnO₂, the composites possess higher capacitance, which is due to an increase in electrical conductivity of the composites. The enhancement of electrical conductivity is due to the appearance of VACNT and conductive networks. Additionally, the composite showed a superior cyclic stability at high current comparing with pure MnO2. Therefore, the introduction of VACNTs into metal oxides can effectively improve their electrical conductivity, and the resulting composites have excellent electrochemical performance as energy-storage materials.

3.1.2 Rechargeable metal-ion batteries

3.1.2.1 Lithium (Li)-ion batteries

Since Li-ion batteries are commercialized by Sony in 1991, they have become the main rechargeable battery

[48]. Compared with traditional rechargeable batteries, Li-ion batteries have the advantages of light weight and excellent energy-storage capacity. In recent years, Li-ion batteries have been developed for use in electric vehicles, hybrid electric vehicles, and other fields [49]. However, to meet these continuously growing performance requirements, current Li-ion batteries need to be improved. Liion batteries are mainly composed of the Li⁺ intercalation anode, cathode, and electrolyte. In the process of charging, Li⁺ ions move from the cathode to the anode and discharging in the opposite direction. The performance of electrode material in Li-ion battery not only affects the energy density and power density of the battery but also influences the cycle life and safety of the battery. Therefore, it is crucial to develop electrode materials with excellent performances for Li-ion batteries.

Due to their characteristics of high SSA, high charge transport capability, and high electrolyte accessibility, CNTs have been studied as electrode materials for Li-ion batteries. Some reports have successfully used MWCNTs and single-walled carbon nanotubes (SWCNTs) as the anode materials of Li-ion batteries. In the literature, it has been reported that the researchers have obtained up to 400 mA h g⁻¹ reversible Li intercalation capacities for MWCNT [50]. Compared with the capacity of graphite (370 mA h g⁻¹), the capacity of CNTs is higher, which is mainly attributed to the high SSA of CNTs. Although excellent performance is achieved when using CNT as anode electrode material, the following problems such as a higher reversible Li storage capacity and stable cycling performance still need to be solved. To solve the above problems, Wang et al. [51] attempted to improve the charge transfer capability of the electrodes by preparing the high-purity VACNTs and demonstrated a high reversible Li storage capacity of 950 mA h g⁻¹ and stable cycling performance during repeated insertion and extraction of Li. Figure 7(a) demonstrates the energy-storage mechanism diagram of VACNTs as electrode materials for Li-ion batteries. It can be indicated from the figure that good electrical conductivity, considerable SSA, and large pore volume are the keys to obtain high Li storage capacity and stability. Figure 7(b-e) shows the electrochemical performance of aligned MWCNTs as the anode material in a Li-ion battery. An increase in the specific capacity with an increase in the cycle number is observed. This can be contributed to the nanometer-sized pore structure of CNTs and short diffusion distance for the Li⁺. Recently, some researches indicated that the VACNTs can make better contact with the current collector and increase the diffusion rate of ions, thus further improving the rate capabilities. For example, Finke et al. [52] studied

Table 2: Summary of electrochemical performance of VACNT and composites for SCs

Electrode materials	Substrates	Carbon sources	Temperature (°C)	Electrolytes	Surface capacitance (mF cm ⁻²)	Specific capacitance (F g ⁻¹)	Retention (%)	Power (kW kg ⁻¹)	Energy $(\mathbf{W} \mathbf{h} \mathbf{kg}^{-1})$	Catalyst	Synthesis methods
VACNT	Si	C ₂ H ₂	850	PVA-KCI	45	Ι	92	Ι	Ι	Fe	PECVD [34]
VACNT-CFP	Carbon	C_2H_4	750	NaCl	6.7	I	06	I	ı	Al + Fe	CVD [35]
VACNT	Al foil PDMS	C ₂ H ₄ C ₂ H ₂	645 750	TEABF ₄ PVA-H ₃ P	1 1	61.2 29.2	93.5 91.3	0.14	76.9 2.4	Fe + Co Fe	CVD [36] CVD [37]
sheet VACNT-	SiO ₂	C_2H_4	800	КОН	I	106.2	95	1.3	5.2	Ferrocene-xylene	CVD [38]
graphrene VACNT-TiO ₂	Stainless	C_2H_2	750	H ₂ SO ₄	16	1	66	2	ı	Al + Fe	CVD [39]
VACNT-CNF Co ₃ O ₄ / VACNT	Si Porous material	C ₂ H ₂ C ₂ H ₄	750 700	EMIBF ₄ KOH	1 1	207 87	95.6	_ 13.6	63.7 36	– Ferrocene–xylene	CVD [40] CVD/thermal annealing [41]
VACNT MnO ₂ /	:S	C ₂ H ₂	720	Na ₂ 50 ₄	I	642	I	I	I	Ferrocene–xylene	PECVD [42]
VACNT VACNT MnO ₂ /CNT PANI/VACNT	Ni Si Conductive film	C ₂ H ₂ C ₂ H ₄	800 750 —	Et4NPF6 — PVA-H ₂ SO ₄	_ _ 192	25 199 _	– 92 66.4	I #	26.7	Ferrocene FePc —	CVD [43] CVD [44] In situ [45]

PVA: poly(vinyl alcohol); CFP: carbon fiber paper; TEABF₄: Ammonium tetraethyl tetrafluoroborate.

the electrochemical properties of VACNTs prepared by pyrolysis for the anode of Li-ion batteries. And they found that the VACNTs are arranged along the ion diffusion direction, which further increases the contact between electrode and electrolyte, further improving the specific capacity and rate performance of the Li-ion batteries. Furthermore, the close contact between the VACNTs and the metal current collector allows the entire electrode to be effectively connected. Therefore, VACNTs with a large SSA and an excellent rate performance are expected to be developed in high-power Li-ion batteries.

3.1.2.2 Na-ion batteries

Despite the growing demand for Li-ion batteries in different electronic equipment, the relatively low content and irregular distribution in earth crust, high cost of Li resources, and further development are restricted [53]. Based on the high abundance, low cost, and suitable redox potential ($E^0_{(N\vec{a}'/Na)} = -2.71 \, \text{V} \, vs$ standard hydrogen electrode), the Na-ion batteries also hold much promise for energy-storage applications [54]. However, studies in recent years have shown that Na-ion batteries are deficient in electrochemical performance, including low energy and power density, low coulombic efficiency for the first time, and short lifetime. Being similar to the energy-storage mechanism of Li-ion batteries, Na⁺ is removed from the positive (cathode) and embedded in

the negative (anode) material through the electrolyte during charging; meanwhile electrons are transferred from the external circuit to the negative to maintain charge balance, whereas the opposite occurred during discharge. Based on the mechanism of energy storage (Figure 8(a)), electrode materials could be classified as anode and cathode materials, among which CNTs with high SSA, abundant pore structure, and high conductivity become a candidate for anode materials. The structure and chemical properties of CNTs generally determine the Na⁺ storage and reaction kinetics, mainly due to the following points [55]: (1) Na⁺ can fill in pores to realize ions rapid diffusion and storage, resulting in excellent electrochemical performance and (2) Na⁺ can also adsorb on the surface or near surface of CNTs: thus the introduction of functional groups and defects on the surface of CNTs can be used as active sites for Na⁺ adsorption to further enhance the electrochemical reactivity. Recently, Hou et al. [56] designed a 3D VACNT framework as the anode material of Na-ion battery and demonstrated a high capacity (356 mA h g^{-1} at 0.1 A g^{-1}) and long cycle life. This unique 3D structure has a larger SSA, facilitates Na-ion transport, and accommodates volume expansion during the cycle. In addition, Guo and coworkers [57] reported the case of heteroatom-doped VACNTs as the anode of Na-ion batteries. The analysis shows that the reversible capacity after 10,000 cycles is $150 \,\mathrm{mAhg}^{-1}$, and this structure provides a good mechanical stability for the rapid insertion and disinsertion of Na ions. Figure 8(b-d) shows the excellent electrochemical performance

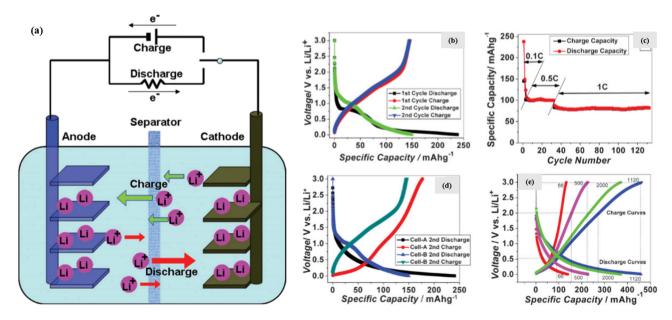


Figure 7: (a) Mechanism diagram of VACNTs as electrode materials for Li-ion batteries [51]. Copyright 2016, Wiley. (b) First two cycles of charge—discharge plots of cell at 0.1 C. (c) Cycling stability of cell at different rates. (d) Comparison of the second-cycle voltage—capacity plots of a different cell. (e) Voltage—capacity plots of cell at different cycles [52]. Copyright 2019, Wiley.

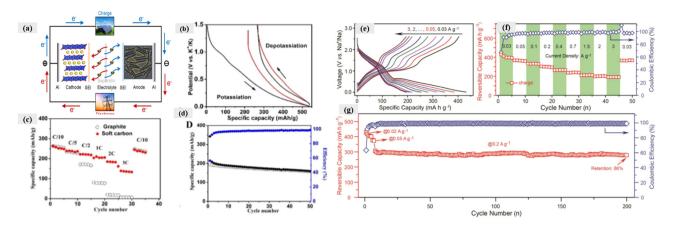


Figure 8: (a) Principle of rechargeable Na-ion batteries [55]. Copyright 2017, Elsevier. (b) GPD profiles of carbon for the initial two cycles. (c) Rate performance of carbon, and (d) cycling stability of carbon at 2C [57]. Copyright 2018, American Chemistry Society. Electrochemical performance of the MnSe@N-CNTs electrode in Na-ion half cells. (e) The GCD curves and (f) rate capability at different current density. (g) Cycling performance at 0.2 A g⁻¹ after the first seven cycles at a low current density [64]. Copyright 2016, Royal Society of Chemistry.

of the MnSe@N-VACNT electrodes in Na-ion half battery. As shown in Figure 8(d), the MnSe@N-VACNT electrode demonstrates superior cycling stability and high efficiency. Moreover, the outstanding rate capability has also been exhibited. The above analysis indicates that VACNTs have the following merit when used as anode materials for Na-ion batteries: (1) As a strong absorbent, VACNTs prevent the active polymer material from dissolving into the electrolyte. (2) The unique structure of VACNTs can form a stable electrode structure and provide an effective conduction path for electrons. (3) VACNTs can contain many active polymers because of their large SSA and abundant pore structures. Although VACNTs have many benefits used in Na-ion batteries, the energy density and cycling lifetime should be further improved. Therefore, the structure and surface chemical properties of VACNT need to be appropriately optimized.

3.1.2.3 K-ion batteries

Compared with Na, the standard reduction potential (–2.93 V) of the resource-abundant K (which occupies 1.5% of the weight in the crust) is lower and close to that of Li (–3.04 V) [58], so it can achieve higher energy density and fast ion transport on K-ion batteries. In recent years, different anode materials have been researched in K-ion batteries, for instance, carbon nanomaterials [59], organic compounds [60], and so on. Among these materials, VACNTs with the following excellent performance have attracted extensive attention:

- 1. The unique conductive network structure provides the conditions for the rapid charge transfer of active materials and metal ions.
- 2. The suitable pore structure provides a good opportunity for electrolyte penetration and ion diffusion.
- 3. Because of its high conductivity, it is used for flexible, lightweight electrode materials without the need for additional conductive agent.

Recently, Li et al. [61] prepared the K-aligned CNT membrane anode by using a mechanically stable, highly conductive VACNTs membrane to store metal K by molten perfusion. Furthermore, its array structure can improve the wettability of liquid K. In addition, compared to conventional copper [62] and aluminum foil [63], its large pore capacity and unique aligned structure provides enough space to store K and for excellent cyclic stability. It is well known that the Stokes radius of K (3.6 Å) is smaller than that of Na (4.6 Å) and Li (4.8 Å), which makes K ions have better ion mobility and conductivity in the electrolyte. However, its atomic radius (1.38 Å) is larger than that of Na (0.97 Å) and Li (0.68 Å), which restricts the diffusion of K ions in the electrode [64]. In Figure 8(e-g), the characterization and electrochemical test have been exhibited. It can be seen from Figure 8(g) that the cycling stability of CNT-based K-ion battery needs to improve in future. As a result of poor diffusion capacity of K ions, it is difficult to obtain high-rate performance for the insertion/ejection of pure K. Therefore, increasing the SSA of VACNTs or introducing heteroatomic/functional groups on the surface of VACNTs will facilitate the rapid diffusion of ions and maintain good

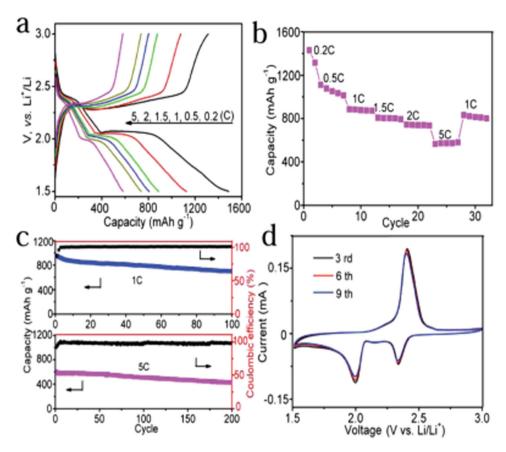


Figure 9: Electrochemical performance of VACNTs@CNFs-S for Li-S battery between 3 and 1.5 V *versus* Li⁺/Li: (a) charge-discharge voltage profiles and (b) rate performance at different current densities [70]. Copyright 2017, American Chemical Society, (c) cyclic stability test at 1 and 5 C, and (d) CV curves [71]. Copyright 2015, Royal Society of Chemistry.

structural stability, thus further enhancing the rate performance and long cycling performance.

3.2 As host materials in energy storage/conversion applications

3.2.1 Li-sulfur (Li-S) batteries

Li–S battery is considered as a promising electrochemical energy-storage system for its high theoretical capacity (1,680 mA h g⁻¹), high energy density (2,600 W h kg⁻¹), and low cost. Unfortunately, its practical application is mainly affected by such factors as low sulfur utilization rate, low power density, and fast capacity attenuation [65]. The current solution is to limit the sulfur to porous carbon-based materials, thereby reducing the loss of Li polysulfide, increasing the conductivity, and adapting to volume expansion [66]. Based on this point, Pan *et al.* [67] using VACNTs and GO produced a Li–S battery with a

specific capacity of up to 800 mA h g⁻¹ at a current rate of 0.1 C and an open-circuit voltage of 3.2 V. Moreover, Zhang and coworkers [68] also developed a Li–S battery using VACNT-graphene and binder-free sulfur composites as dopes. Studies have shown that the sulfur load is about 2 mg cm⁻², and its volume capacity of the battery is 440 mA h L⁻¹. However, the main problem that needs to be addressed is the sulfur loading. Because the energy density of Li–S batteries is proportional to the mass loading of the active material. Based on this question, Chen and coworkers [69] reported a carbon–sulfur nanoarchitecture that encapsulated sulfur particles in hollow VACNT-carbon nanofibers.

In addition, the electrochemical performance diagram of the VACNTs@CNFs-S cathodes is shown in Figure 9. The charge–discharge performance of VACNTs/CNFs-S at the voltage range of 1.5–3 V is shown in Figure 9(a). In the discharge process, we can obviously observe two plateaus of 2.4 and 2.1 V. This is caused by the formation of long-chain Li_2S_x (4 \leq x \leq 8) and short chains Li_2S_2 and Li_2S , which is further indicated the typical behavior of sulfur

cathodes [70]. Furthermore, Figure 9(b) demonstrates that the reversible capacities of the aligned hierarchical nanomaterials are 1,313, 1,078, 878, 803, and 739 at different current densities, respectively. The cycling curves of the electrode at 1 and 5 C are shown in Figure 9(c). After 100 cycles at 1C, its reversible capacity is still as high as $700 \,\mathrm{mAh\,g^{-1}}$ and after 200 cycles at 5 C, the capacity retained 430 mA h g⁻¹. These performances of VACNTs/ CNF-S-based Li-S battery are better than that of traditional C-S cathode [71]. This excellent performance can be attributed to the unique hierarchical structure of VACNTs/CNFs, which can improve the electrical conductivity and effectively regulated the expansion/shrinkage of sulfur volume in the process of lithiation/delithiation; meanwhile, it can also shorten the transport path between Li ions and electrons.

3.2.2 Metal-air batteries

Rechargeable metal—air batteries have a high theoretical energy density, which indicates that they can be widely used in energy-storage systems [72].

3.2.2.1 Li-air batteries

Among these batteries, Li-air batteries are widely investigated because of their theoretical specific energy density of up to 3,500 W h kg⁻¹. However, the batteries may cause side reactions and low recyclability in the surrounding air. Based on this issue, Zhang et al. [73] prepared Li-air battery using VACNTs as air electrode and gel polymer as the solid electrolyte. At a current density of 1,400 mA g⁻¹, the battery has a discharge capacity of 12,470 mA h g⁻¹ and can operate effectively 100 cycles in the air. Liu et al. [69] developed a "break-up-the-wholeinto-part" system for building flexible Li-air batteries that avoids cracking when bent or folded. Analysis shows that the gravimetric and volumetric energy densities of the Li-air battery are 294.68 W h kg $^{-1}$ and 274.06 W h L $^{-1}$, respectively, based on the whole device. The addition of VACNTs can not only provide more stable interconnection between the active material and the electrode but also improve the fast oxygen-electrolyte diffusion [74]. Ji and coworkers [75] designed a 3D hierarchical structure of transition metals doped VACNTs/CNFs with high flexibility and mechanical strength for hybrid Li-air batteries, and the results are shown in Figure 10. In practical tests, the doped VACNTs/CNFs electrode showed a long cycle life (over 120 h), a low overpotential (0.15 V), and a

high voltage (3.4 V), indicating that it has a good prospect for energy-storage applications. The mechanism diagram of the hybrid Li-air battery is shown in Figure 10(a). It is worth noting that this hybrid battery has a voltage of up to 3.4 V, which can power LEDs after charging, showing commercial application value (Figure 10(b)). Figure 10(c and d) shows the charge-discharge curve of the hybrid battery with different cathodes, the relationship between current density and charging and discharging voltage and the cycling performance of the battery in the room temperature, respectively. Figure 10(e) shows the overpotential, which is much lower than that with pristine CNTs (1.46 V), indicating that the RuO₂@VACNT cathode demonstrates superior oxygen reduction reaction (ORR)/oxygen evolution reaction (OER) catalytic activities over CNTs. Furthermore, cycling performances of Li-air battery are shown in Figure 10(h). The cycling stability of RuO₂@VACNT is superior to the pristine CNTs.

These excellent performances are mainly attributed to the following aspects: (1) This unique hierarchical porous structure allows rapid transport of oxygen and electrolytes and (2) VACNTs with high electrical conductivity and interconnect carbon fibers without binder provide good channels for electron transport. Therefore, the hierarchical structure of transition metals doped VACNTs/CNFs is a promising electrode material for hybrid Li-air batteries with low overpotential, high voltage, and high stability. Although Li-air batteries with VACNTs as air electrodes have been widely studied, further optimization of existing electrodes will be required. For example, the performance of Li-air batteries could be dramatically improved by using rationally designed oxygen electrodes with well-defined hierarchical structures and heteroatomdoping-induced catalytic activities, which represents a significant advance in the research and development of Li-air batteries and other energy devices.

3.2.2.2 Other types of metal-air batteries

Zinc–air (Zn–air) battery is widely used because of its advantages of high theoretical energy density, friendly environment, and low price [76]. Xu *et al.* [77] developed a rechargeable Zn–air battery with outstanding electrochemical performance and fiber shape by designing aligned and cross-stacked VACNTs. The energy and power density of the battery were calculated to be 6 A h L⁻¹ and 5.7 W h L⁻¹, respectively. Furthermore, when the battery is bent at different angles (30, 60, 90, and 120°), its structure is not damaged, indicating that the battery has good flexibility. VACNTs with highly active sites and layered porous

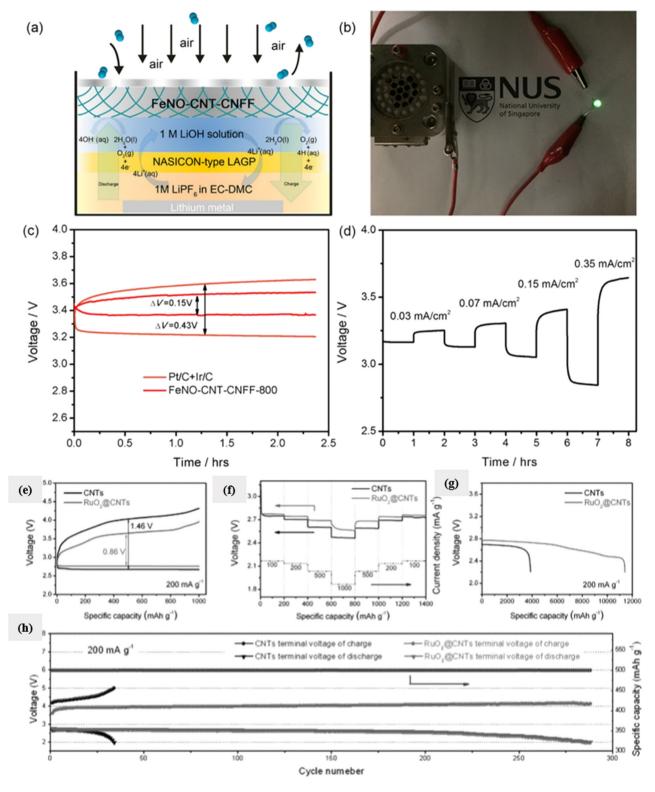


Figure 10: (a) Mechanism diagram of rechargeable Li–air battery. (b) The picture indicates that a green LED (>3 V) can be lightened by the FeNO-VACNT-CNF-based hybrid Li–air battery. (c) Comparison of charging and discharging voltage difference between different catalysts in Li–air batteries. (d) Charge–discharge curves of FeNO-VACNT-CNF-based hybrid Li–air battery at different current densities [74]. Copyright 2017, Royal Society of Chemistry. Electrochemical performances of Li–air battery: (e) first discharge curves at a current density of 200 mA g⁻¹, (f) rate capacity curves at different current density, (g) first discharge curves at a current density of 200 mA g⁻¹, and (h) cycling performance [75]. Copyright 2017, American Chemical Society.

scaffolds prepared by doping or activation methods will exhibit some structural defects, and this unique structure will further enhance the bifunctional activity of ORR and OER. For example, Cai and their group [78] reported that a metal-free air cathode based on VACNTs functionalized with N, P heteroatoms doped carbon. Figure 11(a) shows the synthesis process of NP-VACNT-GF samples. Morphological characterization diagram of VACNT-GF is represented in Figure 11(b and c). The SEM and TEM images of pristine VACNTs show that they are vertically aligned on a 3D GF surface with a diameter of 5-10 nm and length of 5-6 µm. To evaluate the ORR catalytic activity, CV tests were first conducted on NP-VACNTs-GF, COOH-VACNTs-GF, and 40 wt% Pt-C catalyst as a reference in nitrogen-saturated and oxygen-saturated electrolyte. As shown in Figure 11(d-f), a rechargeable Zn-air battery containing a polished Zn anode and an air-cathode based on FeNi/N-VACNT electrocatalyst are assembled. The as-prepared battery achieved a high $V_{\rm oc}$ of 1.48 V (Figure 11(e)), which is much higher than that of Zn-air battery based on Pt-C + IrO₂ (1.4 V). These excellent performances mainly come from the unique structure of the VACNTs. In addition to Zn-air batteries, VACNTs can also be used in aluminum-air (Al-air) batteries with high theoretical energy density. Xu et al. [68] describe a new all-solid Al-air battery with an air cathode composed of VACNTs/silver nanoparticle sheets. The porous structure of VACNTs promotes the diffusion of gas and the transport of electrons, thus improving the electrochemical performance of the battery, such as an energy density of 1,168 W h kg⁻¹. In addition, the Al–air battery can be woven into a variety of textiles for large-scale applications. The electrochemical performance of metal—air batteries supported by VACNTs and other nanomaterials is mainly determined by the conductivity, mass load, and oxygen permeability. VACNTs have high conductivity and excellent electrocatalytic properties, which can better characterize the performance of batteries. Table 3 summarized the applications of VACNTs as host materials in rechargeable batteries.

3.3 As active material in energy conversion applications

Carbon nanomaterials, especially CNTs with excellent performance and their derivatives, are widely used in the field of solar cells. Next, we summarize the research and development of carbon nanomaterials and nanotechnology in the field of energy conversion.

3.3.1 Polymer solar cells

In the past few decades, the preparation methods of materials used to prepare dispersed heterojunction organic solar cells have made progress. In recent years, to further improve the performance of organic photovoltaic devices, more advanced hybrid nanostructures were researched. There are reports [82] that show the electron mobility of CNTs can be as high as 77,000 cm² V⁻¹ s⁻¹, which can be attributed to the high conductivity of CNTs. In fact, the

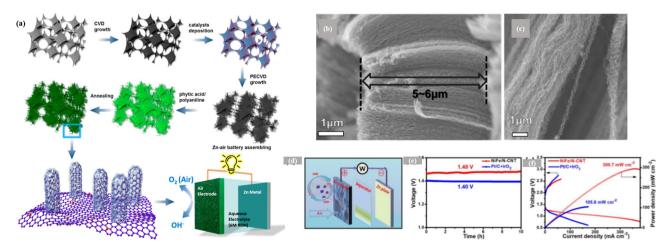


Figure 11: (a) Synthesis process of NP-VACNTs-GF samples. Morphological characterization diagram of VACNT-GF: (b) SEM images of VACNT-GF at low magnification. (c) SEM images of VACNT-GF at high magnification [78]. Copyright 2019, American Chemical Society. (d) Schematic of the Zn-air battery. (e) Open-circuit plots of Zn-air battery based on the NiFe/N-VACNT catalyst. (f) Charge-discharge polarization curves and the corresponding power density [76]; Copyright 2015, Elsevier.

Table 3: A summary of applications of CNTs as host materials in rechargeable batteries

Battery style	Battery style Electrode materials Discharge voltage plateau $\left(V\right)$	Discharge voltage plateau (V)	Mass loading Electrolyte (wt%)	Electrolyte	Specific capacity Cycle life (mAhg ⁻¹)	Cycle life	Current density	Refs
Li–S	VACNT@CNFs-S	2.1	55	1	878	ı	1.0	[44]
Li—S	rGO/VACNT/S	2.1	45	LiTFSI +DME LINO ₃ .	1,255	1	ı	[89]
Li–S	S-VACNTs	2.0	23–50	LiTFSI + DME + LiNO ₃	712-520	80% (100 cycles)	I	[69]
Li-air	VACNT	2.4	0.15 mg	LITF + TEGDME + PVDF-HFP + NMP	12,470	74.1% (30 cycles)	$1,400~{ m mA~g}^{-1}$	[71]
Li-air	FeNO-CNT-CNFFs	3.4	I	KOH + LiOH	30	120 h	I	[73]
Li-air	N-doped VACNT	>1.3	ı	LiClO ₄ + EC	1,814	ı	$0.05~\mathrm{mA~cm}^{-2}$	[75]
Li-air	N-doped VACNT	2.65	ı	LiTFSI	998	ı	$75~\mathrm{mA~g}^{-1}$	[77]
Li-air	N-dopedVACNT	2.0	I	LiCIO ₄ /TEGDME	1,814	I	$0.05~\mathrm{mA~cm}^{-2}$	[62]
Zn-air	VACNT sheet	6.0	ı	PVA + KOH	ı	30 h	ı	[80]
Zn-air	VACNT-GF	0.2	I	КОН		145 h	$20~\mathrm{mAcm}^{-2}$	[81]

NMP: N-methyl-2-pyrrolidone.

thickness of organic solar cells is approximately 100 nm, which is limited by light absorption and diffusion under certain carrier mobility. A simple model indicated that composites with higher carrier mobility properties enable thicker devices to absorb more photons while minimizing charge loss through rapid charge diffusion/collection [83]. Therefore, CNTs with a higher electron mobility are regarded as an alternative material to improve the performance of solar cells. In 1996, Zhou et al. [84] reported the first heterojunction between MWCNTs and a commercially available derivative of polypyrrole (PPv). Kymakis and Amaratunga [85] have prepared CNT/polymer composites on an indium tin oxide (ITO)-coated quartz substrate and demonstrated that when the concentration of nanotubes is low, the photovoltaic behavior is also shown in the range of 0.7-0.9 V of an open-circuit voltage. The performance of this device is improved mainly because of the large SSA, high conductivity, good mechanical stability of the CNTs. Although CNTs can be used in photovoltaic devices to improve the transmission and dispersion of charge [86], they do not contribute much to the performance of the overall photovoltaic cell devices.

To solve this problem, the researchers used VACNTs instead of nonarrays CNTs and polymer composites to form heterojunction and use them in solar cells [87]. VACNTs can provide suitable charge-collection paths due to the large SSA, thus making the charge separation more efficient. Moreover, the layer spacing between VACNTs is matched with the exciton diffusion range, so that the charge recombination between the VACNTs and the polymer interface can be reduced [88]. In addition, the vertical arrangement of CNTs also enables the VACNT/polymer photovoltaic cells to be globally positioned through a common electrode. Although there are not many researches on VACNTs in solar cells, we believe that there will be more development of VACNT-based organic solar cells in the next few years.

3.3.2 Dye-sensitized solar cells (DSSCs)

DSSC is a new type and low-cost solar cell, which mainly imitates the principle of photosynthesis [89]. It is mainly composed of nanoporous semiconductor film, dye sensitizer, redox electrolyte, counter electrode, and conductive substrate. In the early years, the preparation process of DSSC is as follows: First, a tin oxide-coated glass plate doped with fluorine (FTO glass) is used as the anode and a porous thin layer of titanium dioxide (TiO₂) is deposited on it. Second, TiO₂ film coated with dye can be obtained by immersing the plate in a mixture of photosensitive

ruthenium-polypyridine dye and solvent. Finally, a thin conductive sheet covered with a thin layer of electrolyte is used as the counter electrode and sealed with the anode, and the mechanism diagram is shown in Figure 12(a) [90]. When sunlight enters the cell through the transparent FTO glass, it forms an excited state on the TiO2 film surface to inject electrons directly into the conducting band of the TiO₂ semiconductor. Then the dye sensitizers on the TiO₂ surface are then reduced by the electrolyte, and the relay molecules are diffused to the counter electrode. Figure 12(b-e) shows the outstanding performance of the DDSC based on VACNT composite electrodes [91,92]. This result demonstrates that the doping of VACNT with porous and defect-rich activated charcoal is beneficial for the improvement of electrocatalytic activity. In addition, compared to most traditional solar cells, DSSCs can not only work in cloudy skies but also collect energy in an indoor environment. However, the energy conversion efficiency of DSSCs are still lower than that of silicon solar cells. Therefore, the charge loss of photoelectron in the process of anode transmission is the key problem for the further application of DSSC. To solve the charge loss problem, the researchers tested several methods for charge-transport characteristics. For example, the combination of carbon-based nanomaterials, especially CNTs, with anodes may be a promising but challenging way. Recently, some studies have shown that VACNTs coated with TiO2 can generate very fast photocurrents, and further demonstrate that carbon tubes can be used as electrodes in solar cells. Memon et al. [90] reported the preparation of DSSC on the fabric counter electrode by using acid functionalized vertically aligned multiwall CNTs (VAMCNTs) with high conductivity to modify mesoporous activated carbon. The carbon composite materials with high porosity and oxygen-rich surface have a low charge transfer resistance and a good electrocatalytic activity. The obtained photovoltaic conversion efficiency of linen fabric-based DSSCs using gel electrolyte was 6.26%. From the above discussion, we found that the use of the VACNT in DSSC may be attributed to the following two aspects: on the one hand, VACNT as a scaffold can be used as a substrate for dye adsorption. On the other hand, the VACNTs can provide a direct electron-transfer path from the dye coating to the CNTs, thus reducing the series resistance of TiO2-based VACNT DSSCs.

3.4 As a catalyst in a fuel cell application

Fuel cell, which consists of the anode, electrolyte, and cathode, is a device that converts chemical energy directly into electricity. Although there are many different types depending on the electrolyte materials [93], the basic mechanisms are consistent. The basic process is as

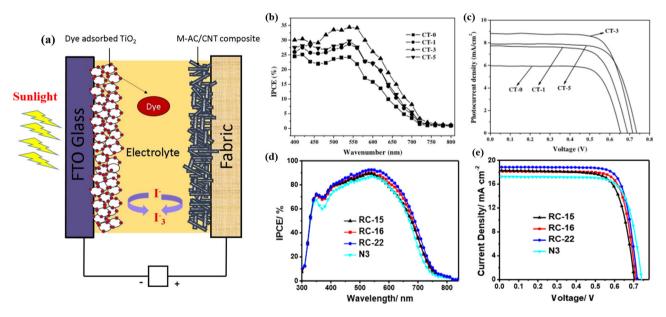


Figure 12: (a) Schematic of the working principle for the DDSC [90]. Copyright 2017 International Solar Energy Society. (b) Comparison of cyclic voltammetry of conventional Pt and as-synthesized aligned-CNT and mesoporous-activated charcoal (M-AC)/VACNT composite. (c) Current-voltage curves of the DDSC based on VACNT/TiO₂ composite electrodes [91]. Copyright 2008 Institute of Physics Publishing. (d) The incident-photo-to-current efficiency conversion spectra for DSSCs sensitized with the VACNT-based composite electrodes. (e) Current-voltage curves of DSSCs [92]. Copyright, 2016, Royal Society of Chemistry.

follows: The hydrogen is first transported to the anode, where it splits into protons and electrons [94], and then the protons and electrons diffuse through the cell to the cathode. At the same time, electrons are released from the anode and provide electric energy. Eventually, electrons and protons combine with oxygen at the cathode to form water [95]. The ORR at cathode is a key process in fuel cells. It can combine oxygen, electrons, and protons directly into water through a four-electron process, or it can form hydrogen peroxide as an intermediate through a less-efficient process involving two electrons. Currently, platinum (Pt) nanoparticles are considered to be using the most ideal ORR catalyst in fuel cells, mainly because of their low overpotential and high current density. However, Pt-based electrodes suffer from the carbon monoxide inactivation, instability, and high prices, which may affect their further commercial application.

In recent years, researchers have attempted to replace Pt electrodes with CNTs with a high SSA and an excellent electrochemical durability as a catalyst and further reducing the load of metals and improving the catalyst activity. For instance, Bose et al. [96] have reported that the performance of MWCNT-supported catalysts in DMFC is better than that of other carbon-supported catalysts. These results demonstrated that the mass activity of Pt/MWNT catalyst was 14.7 mA mg⁻¹ at 0.7 V compared with dynamic hydrogen electrode. Zhi et al. [97] have also found that SWCNT-supported Pt catalysts exhibit a higher reaction rate compared with traditional Pt/carbon catalysts. This result is due to the high porosity of the SWCNT, which contributes to the diffusion of the reactants and further promotes its interaction with the Pt surface. In addition, durability tests also showed that SWCNTs improved the stability of the catalyst. However, the researchers found that untreated pure CNTs did not have sufficient binding sites to immobilize metal nanoparticles. Fortunately, some studies have indicated nitrogen-doped CNTs can be used as a catalytic support for fuel cells; moreover, these functional groups will convert to more stable structures during the heat treatment. Although the catalytic action of CNT is further improved by the process of doping, it is still slightly lower than that of Pt nanoparticles. Recently, Li et al. [98] have found that nitrogen-doped VACNTs with high SSA and good mechanical stability can improve the catalytic efficiency of metal-free fuel cells. The research indicates that the nitrogen-doped VACNTs have higher catalytic activity and better cyclic stability than Pt/carbon [99]. This is because the nitrogen atoms generate a net positive charge on the adjacent carbon atoms in VACNTs and attract electrons from the anode, further enhancing the catalytic activity. The structure and morphology of

N-VACNTs are shown in Figure 13(a-c). Recently, Borondoped VACNTs have been used as metal-free electrocatalysts for ORR, and they have high electrocatalytic activity, stability, and immunity to carbon monoxide toxicity [100]. Theoretical calculation demonstrated that boron doping enhances the chemisorption of oxygen, which means that it act as a bridge to transfer electrons to chemisorbed O₂ and further promoting the ORR. There are two key aspects for ORR: one is the electrical neutrality of VACNTs is broken to form charged sites, which are favorable for O2 adsorption, and the other is the doped VACNT can efficiently create the metal-free active sites for electrochemical reduction of O2. The above results indicate that doped VACNTs have excellent performance as a metalfree cathode catalyst for fuel cells. Yu and colleagues [101] have also studied that phosphorus and nitrogen codoped VACNTs can show good electrocatalytic activity after the removal of iron catalyst, which can be attributed to the high positive charge density of codoped carbon atoms to balance the strong electron affinity of nitrogen atoms, and the morphology and performances of codoped VACNTs are represented in Figure 13. In terms of the initial and peak potential as well as the current density, the P, N-VACNT electrode is most active among all of the VACNTbased electrodes. This phenomenon can be contributed to the synergetic effect that resulted from codoping of the VACNT with P and N. In terms of current density, the maximum oxygen reduction current density of P, N-VACNT electrode is even higher than that of the commercial Pt-C electrode at about -0.22 V (Figure 13(g)) and is higher than that of the Pt-C/GC electrode at about −0.13 V (Figure 13(h)). The results of the above discussion not only have great influence on the commercialization of VACNT-based fuel cells but also have guiding significance for other catalytic processes. However, to develop VACNTbased catalysts with good activity and durability, its catalytic mechanism and the performance evaluation in practical fuel cells need to be further researched.

4 High orientation and excellent mechanical strength of VACNT for versatile applications

4.1 Application in THz spectroscopy

CNTs have become a candidate material for optical and optoelectronic devices in the new generation of THz field due to their unique structure, high conductivity, high

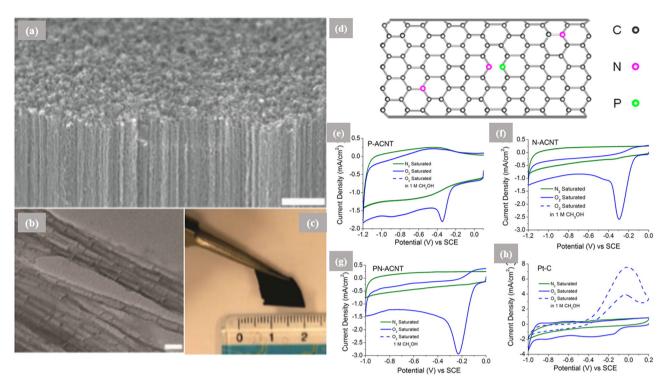


Figure 13: (a) SEM images of the as-synthesized VACNTs on a substrate. (b) TEM image of the purified N-VACNTs. (c) The photograph of the N-VACNT array [100]. Copyright 2012, Wiley. (d) Schematic of the possible P–N codoped VACNT structure. The cyclic voltammograms for the ORR at the (e) P-VACNT/GC electrode, (f) N-VACNT/GC electrode, (g) PN-VACNT/GC electrode, and (h) Pt–C/GC electrode in an aqueous solution of 0.1 M KOH saturated by nitrogen or oxygen gas or an oxygen-saturated 0.1 M solution of KOH upon addition of CH₃OH (1 M) [101]. Copyright 2012, American Chemical Society.

mechanical strength, and excellent photoelectric characteristics. Many experimental and theoretical studies have been carried out to discover various applications of CNTs in THz spectroscopy. For example, He et al. [102] have studied and compared the electrical and optical properties of nonarray single-walled CNTs and multiwalled CNTs (MCNTs) films by a noncontact THz time-domain spectroscopy (THz-TDS). Paul and coworkers [103] have also investigated the application of two commercial nonarray multiwalled CNTs in a THz-TDS. However, researchers found that the interwinding and disorder of nonaligned CNTs will hinder their further application in THz field. Therefore, VACNTs with a high orientation and large aspect ratio exhibit unique optical and electronic properties when applied in the THz domain. Teradal et al. [104] tested VACNT films using THz-TDS and obtained the frequency-dependent complex permittivity and conductivity of several samples. In addition, this property of VACNTs provides an advantage for their research in the field of THz polarization. For example, Ren and coworkers [105] indicated a THz polarizer consisting of VACNTs with ideal wideband THz properties. Furthermore, Paul et al. [106] investigated the application of VACNTs in THz transmission

ellipsometry and revealed the anisotropic characteristics of THz electrodynamics in VACNTs. Figure 14(a) shows the morphology of VACNT and the thickness is about 21.5 µm. The measure device is exhibited in Figure 14(b) where the THz field is oriented perpendicular to the plane of incidence for s-polarization. Recently, our previous studies [107] successfully achieved THz emission by using polarized laser pulses to excite VACNTs. The THz emission of VACNTs showed a more regular response, which laid the foundation for the stable performance of the THz emitter based on VACNTs, and the test results are shown in Figure 14(c-d). The above results indicate that the VACNTs possess excellent structure and performance when used in THz fields. As a noncontact technology, THz-TDS has obvious advantages over other methods, and it seems to provide a useful tool for exploring the photoelectric characteristics of VACNTs.

4.2 Applications in biology and biomedicine

VACNTs with high orientation, excellent electrical, thermal, and spectral properties have also been widely studied in

biological and biomedical fields. For example, it can be applied to biosensors, tissue engineering, and drug delivery.

4.2.1 Biosensor field

Biosensor is an analytical instrument that is sensitive to biological substances and converts their concentrations into electrical signals, which is composed of biological sensitive materials as identification elements, appropriate physicochemical converters, and signal amplifiers. Because of its high surface area and vertical conductive channel, VACNTs can be used as a conduit for biosensor to detect biological species. Moreover, VACNT-based biosensors can immobilize the various recognition molecule without affecting their biological functions, as well as the fast response time due to the efficient mediation of VACNTs in the electron transfer process [108]. For example, VACNTs are used as a sensor element to detect organophosphorus (OPs) (such as acetylcholine [Ach]) compounds that affect

neurotransmitters. However, OPs are bad for the human body because of the restriction of activity of the ACh esterase, which leads to a large accumulation of ACh and series of problems [109]. VACNTs can further enhance the electrochemical reactivity and stability of enzymes due to their high conductivity and orientation, which provide a good supporting effect between the enzyme and the electrode surface. In particular, the fixation of ACh esterase on the surface of VACNTs did not adversely affect their function. Azadbakht et al. [110] synthesized a highly sensitive electrochemical sensor based on VACNTs assembled on a nanoporous gold electrode. It is worth noting that the high sensitivity of these VACNT-based sensors to OPs is mainly attributed to the effect of the good biological activity of the immobilized enzyme on the electrochemical response of the composite electrode. In addition, VACNT-based sensors can also be widely used to detect many other biological molecules including dopamine [111], epinephrine [112], amino acids, and so on. Summarizing the above experiments, we found that the main advantage of using VACNT-based biosensors is that the large SSA of VACNT can provide more

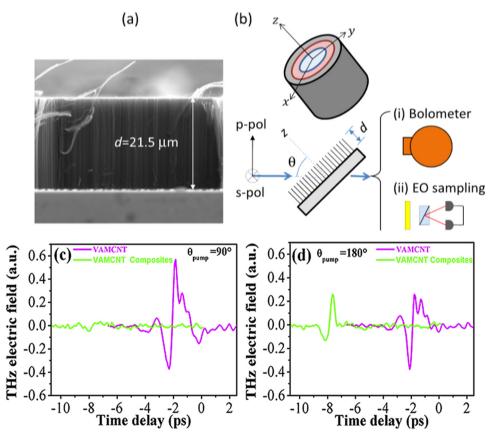


Figure 14: (a) SEM image of the VACNT sample and the film thickness is 21.5 µm. (b) Ellipsometry schematic for THz emission measurements: linearly polarized, broadband pulses are incident upon a VACNT film. THz detection scheme: (i) integrated power spectrum measured with a Si-bolometer and (ii) THz measured with electro-optic (EO) sampling [106] Copyright 2012, American Institute of Physics. (c) Emitted THz domain waveform from the VACNT and the pure quartz substrate. (d) A comparison of the emitted THz waveform from VACNT film and VACNT composite film [107]. Copyright 2018, Elsevier.

fixed sites, and the vertically conductive path can shorten the electron transmission path and facilitate its transmission.

4.2.2 Tissue engineering field

Tissue engineering, also known as "regenerative medicine," refers to the technique of reconstructing or repairing organs and tissues by means of in vitro culture or construction of bioactive substances. In tissue engineering, the scaffold is mainly used to promote the adhesion, growth, differentiation, and proliferation of cells in the 3D matrix, and it must have a certain mechanical strength. In addition, it can also control the position and direction of attached cells to a certain extent. VACNTs with high aspect ratio and inherent mechanical, electrical, and physical properties are considered as a tissue-engineering material for improving the mechanical and electrical performances of artificial tissue scaffolds [113], bone regeneration [114], and other tissue engineering. Im and coworkers [115] designed functional cardiac membranes by implanting neonatal rat cardiomyocytes in VACNT-incorporated photocross-linkable gelatin methacrylate (GelMA) hydrogels. Specifically, there is a three-fold increase in a spontaneous synchronous beating rate of the cardiomyocytes in comparison to original GelMA hydrogel. In addition, the results also showed that the conductive network formed by VACNTs in a porous gelatin framework is the main property of VACNT-GelMA, which can improve the adhesion and coupling of heart cells.

The size, periodicity, and aligned structure of VACNT scaffolds also affect the interactions between cells and

scaffolds [116]. Researchers used VACNTs as a periodic 3D scaffold structure for cell seeding and growth. Mouse fibroblast was then successfully cultured on these periodic matrices. Moreover, bio-hybrid tissue actuator is another application of VACNTs in tissue engineering as shown in Figure 15. In this study, the researchers synthesized a VACNT microelectrode and embedded in flexible and biocompatible hydrogels used them as a scaffold for cellular stimulation and exhibit anisotropic conductivity. The resulting tissue has a uniform structure, and the coupling between the cells is further improved and exhibits excellent mechanical integrity. Meanwhile, the microelectrode array is combined with advanced electrophysiological functions to demonstrate strong muscle shrinkage. The above analysis indicates that the scaffolds implanted in cells should not only match the cell morphology but also systematically study the cell interactions [117]. Although VACNTs cannot be absorbed by living organisms, 3D structures based on VACNT materials have been shown to support cell adhesion and growth, and the materials have no toxic byproducts compared with polymers [118]. In addition, the 3D structure based on VACNTs has integrity and stability and has strong mechanical strength to support tissue development. As these reports suggest, VACNTs can be used as biocompatible matrices to repair or enhance damaged tissue.

4.2.3 Drug delivery field

The goal of drug delivery is to use receptor-functionalized carrier molecules to carry the drug around the body, then

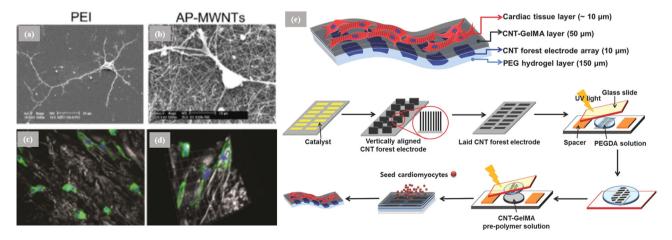


Figure 15: SEM images of neurons grown on polyethyleneimine (a) and MWCNT (b) [116]. Copyright 2015, Wiley. (c) Confocal microscopy images of osteoblasts attached on 10% nHA chitosan scaffold and (d) 3D morphology of attached cells [117]. Copyright 2019, Springer Nature. (e) A diagram exhibiting the synthesis process to produce 3D actuators composed of a multilayer hydrogel sheet impregnated with VACNT microelectrodes [118]. Copyright 2006, Springer Nature.

attach it to the site of the problem and release the drug [119]. Functionalized VACNTs are considered to be targeted carriers of drug delivery and have the following characteristics: (1) each VACNT can be functionalized to detect a cell and interact with them, further increasing efficiency and reducing drug dosage; (2) VACNTs with nanostructures can penetrate cell membranes, making them ideal materials for injecting drugs directly into cells [120]; and (3) the drug could be encapsulated into VACNTs and enter the cells, and the VACNT caps could be chemically decomposed when the drugs are needed to be released [121]. VACNTs need a drug-unloading mechanism (like the change in temperature and pH) in

order to effectively perform their drug delivery function. For example, the intracellular pH was lower than that of the extracellular pH, thus CNTs carrying a large number of drugs entered the cell and were activated to release the drugs it carried. Furthermore, drugs can be released by stimulating with near-infrared wavelengths of light, which are not absorbed by some biological structures. The combination of doxorubicin (DOX) with E2-PEG-MWCNTs not only facilitated nuclear targeting but also deciphered to a synergistic anticancer response *in vivo*. A schematic about *in vivo* photothermal treatment is shown in Figure 16(a). Figure 16(b) indicated the tumor growth inhibitory effect of free DOX/DOX@f-CNTs in sprague-

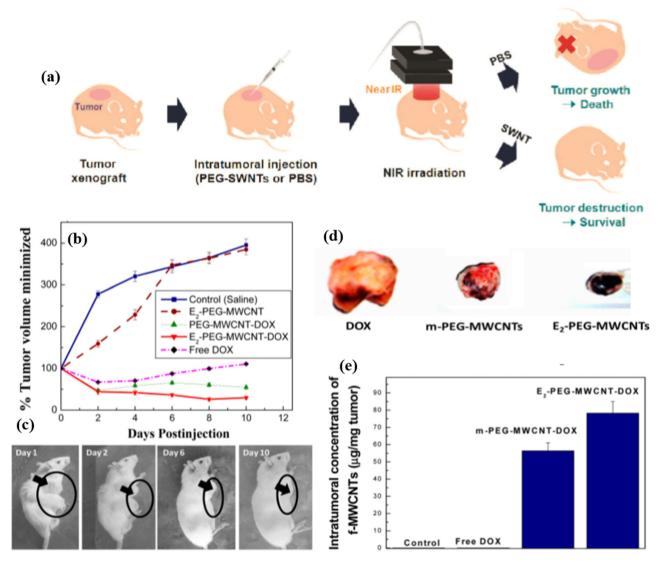


Figure 16: (a) Schematic of the procedure and results of polyethylene glycol-carbon nanotubes (PEG-CNTs)-mediated photothermal treatment of tumors in mice [121]. Copyright 2009, Elsevier. (b) *In vivo* tumor growth inhibition of SD rats intravenously administered with free DOX and various MWCNT preparations loaded with an equivalent amount of the free drug. (c) Typical photograph of tumor reduction in rats treated with DOX@E2-PEG-MWCNTs over time. (d) A photograph and (e) spectrophotometric data of DOX@MWCNTs [122]. Copyright 2013, American Chemical Society.

dawley (SD) rats. Theses photographs demonstrating the reduction of the tumor burden in DOX@E2-PEG-MWCNTstreated rats have been presented as Figure 16(c) [122]. A photograph of excised tumors treated with free DOX/ DOX-MWCNTs. These results indicate that VACNT materials have a great potential for applications in drug delivery.

4.3 Application of environmental sustainability

VACNTs not only play a crucial role in solving energy crisis but also play an important role in solving environmental problems. Although a large number of environmental applications have been proposed for VACNTs, researchers have focused on two main categories, including adsorption and catalysis.

4.3.1 Applications in adsorption

The adsorption process refers to the traditional technique of selectively removing pollutants using special equipment to produce clean and safe water or gases [123]. VACNTs are widely used in adsorptive materials because of their high orientation, suitable pore structure, adjustable nanometer scale, and inherent hydrophobicity [124]. Recently, Liu et al. [125] used N2-adsorbed VACNTs as a model and found that VACNTs had a higher absorption rate than nonarray CNTs by using ultrasonic treatment. This is because of the increased gap between individual nanotubes in the VACNTs. The adsorption applications of VACNTs include liquid adsorption and gas adsorption.

4.3.1.1 Liquid adsorption

The unique geometry of VACNTs enhances the chemical distribution through physical uptake like an adsorbent. Therefore, 3D VACNTs with special structure can be used for liquid phase adsorption of oil cleaning and have good oil absorption performance (about 100 times higher than activated carbon) [126]. In addition to physical factors, chemical modification of VACNTs can also improve its adsorption capacity. For example, Hashim and coworkers [127] synthesized a 3D macroscale nanotube elastic solid directly through a boron-doping strategy during chemical vapor deposition. Studies have shown that the interconnected VACNTs skeletons enhance the absorbability of the oil and enable the adsorbent to be reused. Compared with nonarray CNTs and activated carbon [128], VACNTs have a larger surface area, inherent chemical stability, and mechanical strength that make them easier to absorb. In addition, the high orientation structure can further enhance the adsorption capacity, which is very important for future practical applications.

4.3.1.2 Gas adsorption

Similar to liquid adsorption. VACNTs can also be used as gas adsorbents to remove pollutants that are harmful to human health and the ecosystem (e.g., CO₂ [129], SO₂ [130], and NO_x [131]). Ba and coworkers [132] prepared a double-walled VACNTs (Figure 17(a and b)) and found that the ability of VACNTs to absorb CO2 increased as their diameters decreased under high pressure. To further improve the adsorption performance at low pressure, the authors found that the oxygen plasma could functionalize the VACNTs without affecting the ordered structure, thus improving its adsorption performance and the dynamic CO₂ adsorption. From Figure 17(c), we can find that the adsorption capacity of a 3D VACNTs with a diameter of 5 nm is almost three times that of a VACNT with a diameter of 8 nm. Furthermore, high pressure CO₂ adsorption characteristics of VACNT are shown in Figure 17(d). Although the current researches on VACNTs adsorption are still in the theoretical stage, the advantages of this unique structure as an effective adsorbent have been demonstrated. This advantage can be attributed to the fact that VACNTs have adjustable intertube spacing compared with nonarray CNTs. Furthermore, VACNTs with adsorption properties can also be used for hydrogen storage materials to solve the storage and conversion problems of renewable energy [133]. When El Kady et al. [134] studied hydrogen storage in VACNT, they found that controlling the spacing between adjacent tubes could provide more space for efficient storage of hydrogen. However, the researches on the absorption capacity of VACNTs on H₂ is controversial, which hampers the further development of this technique [135]. Therefore, the future research can be carried out from both theoretical and experimental aspects, so as to realize the efficient storage of hydrogen in VACNTs.

4.3.2 Applications in nonelectrochemical catalysis

VACNTs with high SSA, controlled preparation, chemically uniform active sites and stable geometric structure is widely used in the field of catalysis. However, the

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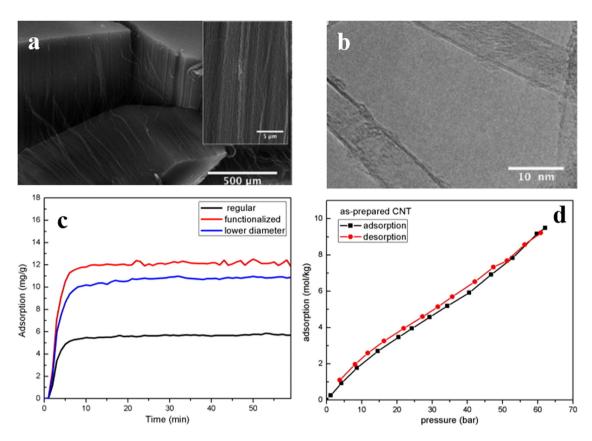


Figure 17: (a) SEM image of 3D VACNT. Inset shows the vertically aligned, highly parallel CNT morphology. (b) TEM image of individual VACNT. (c) Dynamic CO₂ adsorption researches at 1 atm, 308 Kelvin under different conditions. (d) High pressure CO₂ adsorption characteristics of VACNT under different conditions [132]. Copyright 2013, Elsevier.

current catalytic research on VACNTs mainly focuses on electrochemical catalysis (e.g., hydrogen evolution reaction [136], oxygen reduction [137], and carbon dioxide reduction [138]), and the application of nonelectrochemical catalysis is rare. Here we will focus on the nonelectrochemical catalysis of VACNTs. Akhavan et al. [139] synthesized TiO2-VAMCNTs heterojunction arrays as photocatalysts for inactivation of Escherichia coli bacteria under visible light irradiation. Studies have shown that from VACNTs to TiO₂ to TiO₂/VACNTs, their antibacterial activity gradually increases. In addition, VACNTs also play an important role in the control of gas pollutants. And the application of VACNTs in this field is usually a support or limitation to active substances. Based on this point, the researchers synthesized a MnO₂/VACNTs heterogeneous catalyst using VACNTs as a carrier to remove gaseous pollutants. As a supporting carrier, VACNTs can effectively expand the surface area and improve the catalytic performance. With the researchers' attention to the structure of metal oxide catalyst [140], VACNTs with orientation structure and excellent performance provide a good platform for the support and full dispersion of catalyst, which lays a

foundation for improving the catalytic performance of catalyst. The catalytic applications of VACNTs and their corresponding functional composites are shown in Table 4.

5 Conclusions and prospects

In this study, a critical review has been collected to the recent advances of VACNT materials. Various synthesis methods including arc discharge, laser ablation, thermal chemical vapor deposition, and plasma-enhanced chemical vapor deposition have been introduced. In addition, the VACNTs with excellent performance and multiple functionalities have been designed to prove their great potential in energy storage and conversion, catalysis, THz spectroscopy, and environmental sustainability and eventually achieve large-scale production and commercial application. Although remarkable achievements have been made in the application of VACNT materials in the past few years, there are some major challenges that restrict the widespread use of VACNTs.

Table 4: A summary of application of VACNTs in catalysis

Catalytic type	Materials	Catalyst preparation	Reaction type	Reaction type Catalytic application	Ref
Electrochemical catalysis Pt-VACNT-carbon fibers	Pt-VACNT-carbon fibers	The pyrolysis of FePc on the surface of CFs and deposition Pt nanoparticles	ORR	Environment/biological sensor	[141]
Electrocatalysis	N-doped VACNT	Produced by pyrolysis of iron(II) phthalocyanine	ORR	Clean energy; fuel cells	[86]
Electrocatalysis	B/N-doped VACNT	B/N-VACNT were prepared by pyrolysis of melamine diborate	ORR	Fuel cells; biosensor	[1]
Electrocatalysis	VACNT-metal oxides	Prepared by atomized ethanol-assisted osmotic preparation of uniformly coated MOS	ORR	Fuel cells; energy-storage devices	[142]
Electrochemical catalysis	Electrochemical catalysis Molybdenum sulfide/N-doped VACNT	N-doped VACNTs were prepared by PECVD, and immersed in aqueous HER HCl solution and $({\rm NH}_{\rm A})_2{\rm MoS}_4$	HER	H ₂ production	[143]
Electro-catalysis	WC-VACNT	VACNT by hot wire CVD	HER	H ₂ produce	[136]
Electrochemical catalysis N-doped VACNT	N-doped VACNT	$HCON(CH_3)_2 + (C_2H_5)_3N$	CRR	Environment sustainability	[138]
Photocatalysis	NVACNT/TiO ₂	ı	ı	Sensor	[144]
Photocatalysis	TiO ₂ -VACNT-Pt	Photoanodic reaction-photocathodic reaction	Redox reaction	Clean energy	[145]
Photocatalysis	Fe ₂ O ₃ -VACNT	C ₂ H ₆ O-assisted maceration method	SCR	Environment sustainability	[146]
Electrochemical catalysis Mn-Mo-VACNT	Mn-Mo-VACNT	$HNO_3 + C_6H_8O_7 + Mn (NO_3)_2 + MoO_3$	SCR	Environment sustainability	[147]

MOS: molybdenum sulfide; HER: hydrogen evolution reaction.

- (1) The low-cost and high-efficiency preparation of VACNTs is a major challenge. With its adjustable microstructure, excellent mechanical and electrochemical properties, VACNTs can be used in many different fields. However, the gathering of high conductivity, high mechanical strength, and high electrochemical properties in a VACNT is challenging. In addition, the cost of VACNTs should be at an acceptable level to accommodate future large-scale commercial applications. Based on this point, in the future research process, the cost can be controlled by changing the preparation parameters and optimizing the synthesis process so as to make the synthesis process more economical and convenient.
- (2) VACNTs with high orientation, suitable ion-transmission path, high SSA, and high conductivity have been used to solve the problems of nonarray CNTs and other traditional carbon materials in energy storage. Currently, the main issue of VACNTs as a material in the field of energy storage is the balance of energy density, power density, and cycle life. To solve the problem, it is necessary to develop composite electrodes with high capacitance by combining VACNTs with carbon nanomaterials with high surface area, polymers or transition metal oxides, or to combine with high-voltage ionic liquid electrolytes. In addition, VACNT-based rechargeable batteries also need to be further improved. The performance of the battery may be influenced by the electrochemical and mechanical properties of the electrode, as well as the interface properties of the electrode material and current collector. Generally, VACNTs can be used not only as a host anode material but also as a conductive additive for traditional graphite anodes or high-capacity metal oxides to further improve the rate performance and cycling performance of the battery. Additionally, considering the respective advantages of SCs and batteries, one can combine the high-capacity performance of batteries with the outstanding rate-performance and long cycle life of SCs to develop advanced energy-storage devices with high energy and power. In the research of this advanced energystorage devices, VACNTs with good conductivity, high SSA is a good choice.
- (3) VACNTs can provide more available surface area than nonarray CNTs, which can further improve the efficiency and power of the solar cells. Although VACNTs with high electron mobility have been used as an alternative to charge transfer materials in polymer solar cells, their applications in organic solar cells are still in their infancy. The continuous research in this

field may promote the further development of VACNT materials in the field of photovoltaic technology. Furthermore, VACNT materials also have influence for other energy-conversion systems, such as fuel cells. The fuel cell needs a catalyst for ORR, and Pt has a high efficiency in catalyzing this process, so it is considered to be the most suitable fuel cell catalyst at present. However, its unstable performance and high price are challenges for mass production of fuel cells for commercial applications. VACNT-based materials are used as a catalyst/catalyst carrier to replace/load some noble metals in the catalysis field. This can be contributed to their outstanding features including interconnected porosity, high conductivity, mechanical stability, and excellent adsorption performance. However, compared with the Pt-C electrode, pure VACNT is regarded as the catalyst with some existing issues such as low catalytic activities and so on. Therefore, heteroatom-doped VACNTs have been found to be an efficient way to further improve the catalytic activity of VACNTs. For example, N is more electronegative than C, thus the charge density of adjacent carbon atoms can be removed and N-type doping behavior can be introduced. Like N, B is a commonly used heteroatom dopant that acts as a charge donor to the VACNT structure due to its lower electronegativity than C, leading to P-type behavior, which favors catalysis.

- (4) THz pulses are ideal for detecting the microscopic processes of the interaction between light and carbon nanomaterials under the excitation of femtosecond light. Therefore, correctly understanding the THz responses of VACNT materials is the key to understanding the mechanism of ultrafast charge carriers in carbon nanomaterials. However, the current research on VACNT materials in THz mainly focuses on untreated pure CNTs. Therefore, researchers can treat the prepared VACNT materials and compare them with the untreated CNTs, which will help us better study and understand the response mechanism of different carbon nanomaterials in THz fields. In addition, the researchers can further analyze the influence of the interaction between the substrate and the carbon layer from the CNTs grown on different substrates, which provides a foundation for the further study of VACNT materials in THz spectrum.
- (5) In addition, we also discuss the application of VACNTs in biology and biomedicine, especially in biosensors, tissue engineering, and drug-delivery fields. At present, one potential question is whether VACNT materials are toxic for future biomedical applications. Potential side effects of VACNTs and other carbon

nanomaterials have been reported in some reviews. These studies have demonstrated that the main factors affecting the toxicity and safety of carbon nanomaterials are their morphology, transport pathways, and nonspecific adsorption of biomolecules in vivo. Therefore, to reduce the potential adverse effects of carbon nanomaterials, researchers have been looking for various solutions. For example, recent researches suggested that peroxidase enzyme might cause the oxidative degradation of carbon nanoparticles in biological systems. However, few studies have been conducted on the ability of specific tissues in vivo to induce degradation of carbon nanomaterials. Therefore, in the future research, VACNT materials can be studied from the above aspects, so that carbon nanomaterials with unique physical and chemical properties and biocompatibility can be applied in a variety of fields.

The application of the VACNT array with hierarchical structure and anisotropy is expected to change a series of practical application processes and finally achieve sustainable development. However, it has been suggested that the basic concepts and methods of using VACNT advanced materials have some shortcomings, which will hinder the further development of VACNTs in the environment field. Therefore, the future development should not only study the innovative application opportunities of VACNT materials in the environment but also promote the production of materials in a sustainable way.

From the above discussion, we can conclude that the application of VACNT materials in energy storage and conversion, catalysis, THz, biomedicine, and environment is a promising research topic. Advanced VACNT materials' research and development will continue to move forward because of their unique structure and tunable performance parameters, as well as their different roles in different applications. With astonishing advances of characterization techniques, novel theoretical calculation tools, and synergistic VACNT-based electrode material systems, we believe that, all of the as-mentioned issues could be resolved eventually. The significant improvement of the electrochemical and mechanical performance of the VACNT materials could turn them into a viable and economical next-generation high-performance nanomaterials.

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