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# Synthesis of Three-Dimensional Nanocarbon Hybrids by Chemical Vapor Deposition

*Hua-Fei Li, Shuguang Deng and Gui-Ping Dai*

## Abstract

Carbon nanomaterials such as graphene, carbon nanotube (CNT), and carbon nanofiber (CNF) have received tremendous attentions in the past two decades due to their extraordinary mechanical strength and thermal and electrical properties. Recently, it indicates that three-dimensional (3D) nanocarbon hybrids overcome the weakness of individual low-dimensional nanocarbon materials and exhibit unique properties among carbon nanomaterials. Efforts have thus been made to acquire synergistic integration of one-dimensional (1D) and two-dimensional (2D) carbon nanomaterials. Meanwhile, chemical vapor deposition (CVD) is a widespread and effective method of fabricating three-dimensional nanocarbon hybrids compared with other synthetic methods. In this case, a number of 3D nanocarbon hybrids are synthesized by using different precursors at diverse temperature, and the nanocarbon hybrids are expected to be a promising choice for various application areas in the future.

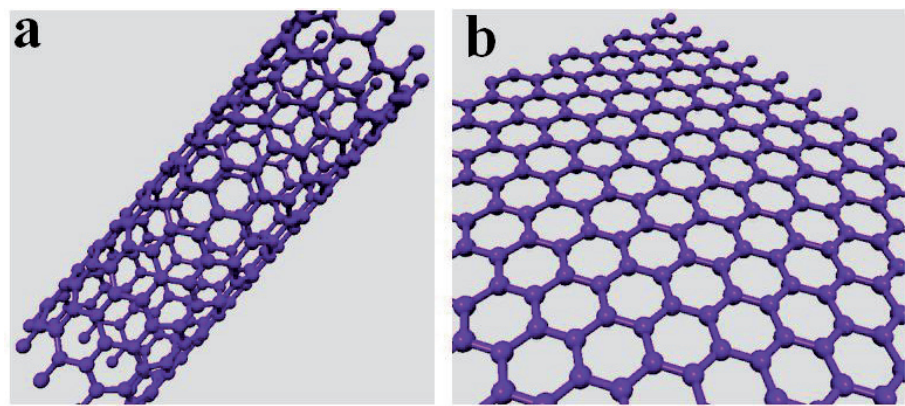
**Keywords:** chemical vapor deposition, three-dimensional nanocarbon hybrids, graphene, carbon nanotube, carbon nanofiber

## 1. Introduction

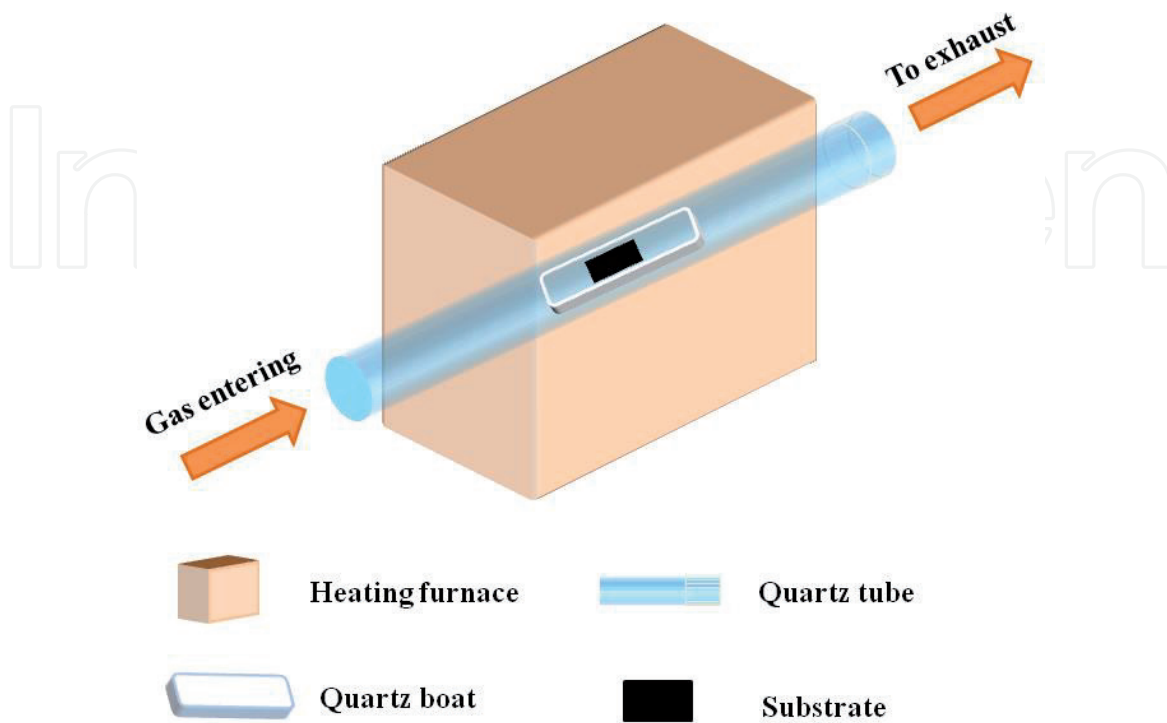
As the typical 1D carbon materials, carbon nanotubes (CNTs) (**Figure 1a**) and carbon nanofibers (CNFs) have been widely investigated in the past two decades because of their merits, such as outstanding mechanical strength, large surface-to-volume ratio, and extraordinary electrical conductivity [1–4]. At the same time, graphene (**Figure 1b**), a recently discovered 2D  $sp^2$  carbon, displays outstanding physical and chemical properties such as high specific surface areas (about  $2620 \text{ m}^2 \text{ g}^{-1}$ ), great lightweight, and fast electron transport kinetics [5–7]. Nevertheless, their physical and chemical performances inevitably decrease compared to the theoretical prediction result from the existence of the van der Waals interaction, generating easy self-aggregation and stacking during the synthesis process [8]. Therefore, the 3D nanocarbon hybrids (such as CNT/graphene, CNF/graphene, CNT/CNF hybrids) are studied by a large number of the research groups, aiming at overcoming these shortcomings and a synergistic integration of their inherent properties in the new hybrid materials [9–11]. These nanocarbon hybrids have an interconnected network of carbon structure, resulting in a synergistic effect in enhanced conductivity in comparison with the individual components,

and the special 3D structure significantly provides a variety of applications, such as field-effect transistors [12, 13], electron field emitters [14–16], sensors [17–20], fuel cell [21–23], batteries [24, 25], and supercapacitors [26–30].

To date, a number of techniques and methods have been utilized for the fabrication of nanocarbon hybrid, such as mixing process of surface-treated carbon materials (including solution processing [31, 32], vacuum filtration [33, 34], layer-by-layer self-assembly method [35, 36]), hydrothermal method [37], multi-step approaches using combinations of decorated carbon materials and CVD [10], and multi-step and one-step chemical vapor deposition [38–48]. Among all the nanocarbon hybrid fabrication approaches reported, CVD techniques are considered as the most versatile and promising way for nanocarbon composite production with reasonable structure and mechanical strength, which has attracted tremendous research attention during the recent decades. As a sophisticated synthesis method for both laboratory research and industry production, conventional CVD (shown in **Figure 2**) is applied in many areas, such as thin-film coating, crystal growth, and



**Figure 1.**  
*Schematic diagrams of graphene and carbon nanotube.*



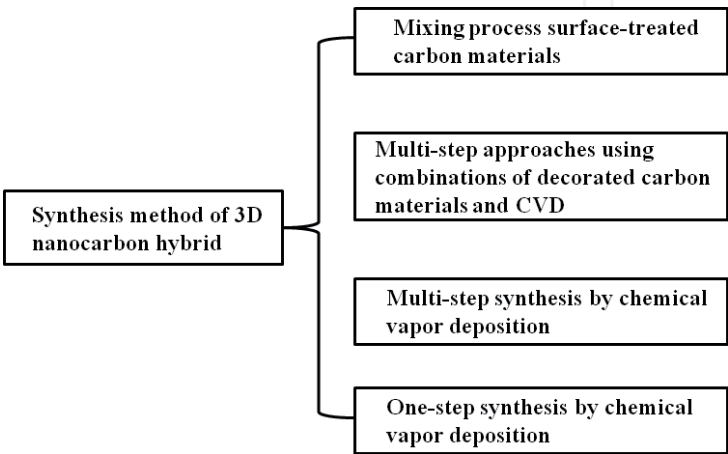
**Figure 2.**  
*Schematic diagrams of CVD technique.*

powder production and also suitable for the synthesis of nanocarbon materials. The mechanism of conventional CVD generally includes two steps, initially thermal decomposition of gaseous precursor [10], organic solvents [47], or solid feedstock [9, 28] and thereafter reassembly of carbon atoms into  $sp^2$  carbon nanostructures under the effective catalysis such as Cu [8], Fe [12], Co [28, 44], Ni [24], or their mixture [11, 49] at high temperature. Compared with other approaches, CVD technique significantly fabricated well-interconnected three-dimensional nanocarbon materials without needing sophisticated chemical routes with solvents and highly toxic agents during synthesis process. Zhu et al. [50] reported that the seamless, covalently bonded three-dimensional nanocarbon architecture was fabricated on the surface of Cu foil via simple two-step CVD methods. It is worth noting that although different aforementioned methods are employed for the production of nanocarbon hybrids, a facile and simple approach for controllable growth of three-dimensional carbonaceous nanomaterials is still a big challenge.

In this chapter, we present a summary of the researches about nanocarbon hybrid in recent years, with a focus on the popular fabrication techniques. Moreover, the merits and demerits and effect of experimental parameters of these CVD methods are presented in detail. Finally, we discuss the development trend, challenges, and performance applications of nanocarbon hybrids in the further.

## 2. Preparation techniques of three-dimensional nanocarbon hybrids

Up to now, varied approaches have been used for the fabrication of 3D nanocarbon hybrids, and the preparation technology generally could be categorized into four different approaches (shown in **Figure 3**): mixing process of surface-treated carbon materials, hydrothermal method, multi-step approaches using combinations of decorated carbon materials and CVD, and multi-step and one-step chemical vapor deposition. In addition, early researches on the construction of 3D hybrids focus on mixing process, which includes solution processing, vacuum filtration, and layer-by-layer self-assembly methods. Compared to other methods, hydrothermal route is an appropriate way to the mass preparation of graphene-carbon nanotube hybrids because of the easy operation and mild experimental environment. Moreover, the composites consisted of carbon nanotube and carbon nanofiber mainly produced by utilizing the multi-step approaches using combinations of decorated carbon materials and CVD method. Especially, multi-step and one-step



**Figure 3.**  
*Classification of 3D nanocarbon hybrids synthesis techniques.*

chemical vapor deposition is considered as a simple and promising way to build 3D hybrids with hierarchical structure and stability.

### 2.1 Mixing process of surface-treated carbon materials

As the early hybridization approaches, solution processing, vacuum filtration, layer-by-layer self-assembly methods, and so on could be classified into the facile mixing process. Altogether 1D carbon nanomaterial incorporation of 2D nanomaterial with a facile mixing process exhibits a synergistic effect in enhanced properties. However, the nanocarbon hybrids are synthesized by utilizing various methods to mix modified carbon-based feedstocks, which generally need sophisticated chemical routes with solvents and highly toxic agents [31, 33–36]. Furthermore, this kind of techniques suffers from poor controllability, leading to the restriction of practical application due to the aggregation and stacking of carbon-based materials [51].

### 2.2 Hydrothermal method

With regard to hydrothermal method, firstly, the carbon feedstocks are dissolved and the mixed solution is transferred into a heating instrument. Secondly, the hydrothermal treatment is performed at low temperature, and the final product is obtained after centrifugation, washing, and freeze-drying process. Although this method has merits of mild conditions and scale-up synthesis, it is not suitable for the industrial production due to the time-consuming fault and defective products. Besides, the obtained 3D nanostructures are chiefly based on weak interconnection between individual nanocarbon components instead of owning powerful bonding, leading to robust 3D architecture [52].

### 2.3 Multi-step approaches using combinations of decorated carbon materials and CVD

Chemical vapor deposition is considered as the most promising approach of the preparation of graphene, CNTs, and CNFs on the substrate surface. Thus, it is always employed to facilitate the growth of CNTs on the decorated carbon materials, leading to the 3D hierarchical composite. For example, most of the reported 3D carbon nanotube/carbon nanofiber hierarchical composites are typically prepared by a multi-step route, which first needs electrospinning technique and post-carbonization for the preparation of CNFs, followed by decorating the CNFs with metal catalyst nanoparticles, and eventually the CNT growth is promoted by using toxic organic gases or solvent as carbon source during the CVD process [10, 22]. This kind of CVD-based methods has distinctive advantages: efficiency, convenience, and high yield. However, the stable and suitable decorated carbon materials that always need sophisticated pretreatment are vital to the construction of 3D carbon hybrids.

### 2.4 Multi-step synthesis by chemical vapor deposition

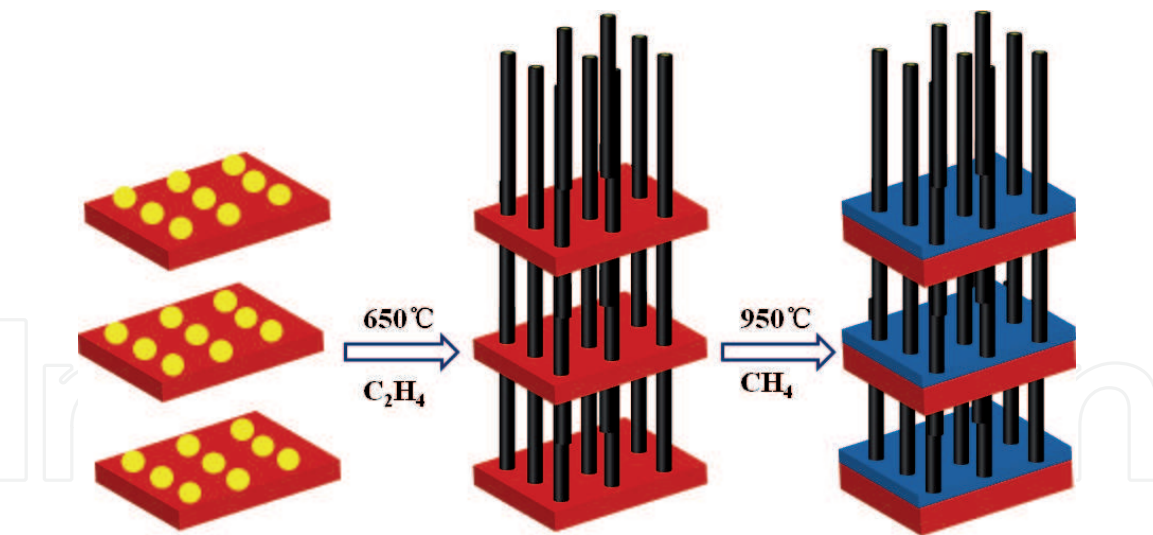
Multi-step chemical vapor depositions have been utilized in recent years to integrate individual 1D with 2D carbon nanomaterials to achieve controllable configurations of 3D nanostructures. Recently, Tang et al. successfully fabricated graphene-carbon nanotube composite on exfoliated vermiculite (EV) substrate by the multi-step CVD method (as shown in **Figure 4**). The whole CVD process could be divided into two steps: firstly, the aligned CNTs are synthesized at 650°C by using  $C_2H_4$  as carbon source, and, secondly, the uniform graphene sheet directly



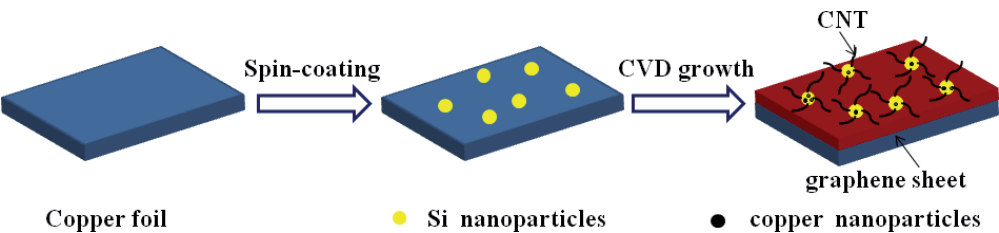
grows on the surface of substrate at a higher temperature of 950°C by utilizing the hydrocarbon—CH<sub>4</sub>, resulting in the in situ synthesis of graphene-carbon nanotube-graphene sandwiches [53]. In other methods of the successful fabrication of 3D hybrids, the obtained component materials are always entangled with each other, and the ordered 3D packing architecture is hardly available. Nevertheless, this multi-step way successfully integrates low-dimensional materials into 3D ordered, controllable, and well-connected structures [50]. Additionally, the morphology and nanostructure could be well controlled by adjusting the experimental parameters due to the separated CVD processes. It is a pity that the multi-step process always requires strict growth conditions and large consumption of power (high temperature) for the growth of nanocarbon materials.

### 2.5 One-step synthesis by chemical vapor deposition

Recently, tremendous efforts have been made to produce 3D nanocarbon hybrid via simultaneously in situ growing of 1D and 2D carbon nanomaterials on the surface of substrate during the CVD method. For example, Dong et al. (illustrated in **Figure 5**) reported that graphene/carbon nanotube hybrids were synthesized by a facile single-step CVD route employing ethanol (C<sub>2</sub>H<sub>5</sub>OH) as feedstock on the surface of Cu substrate decorated with Si nanoparticles, and the property and shape of hybrid could be varied by adjusting the fabrication environment (e.g., Si nanoparticles, temperature, and annealing time). The single-step route has the merits of better electrical conductivity and lesser defect density than the multi-step methods [43]. Additionally, although this one-step process effectively decreases the



**Figure 4.**  
*Scheme for the two-step CVD synthesis of graphene/carbon nanotubes hybrids.*



**Figure 5.**  
*Scheme for the one-step CVD synthesis of graphene/carbon nanotubes hybrids.*

consumption of power, they still need high temperature, flammable gases, or toxic chemicals for the in-situ growth of 3D architecture.

### 3. Effect of experimental parameters of CVD methods

#### 3.1 Effect of catalyst nanoparticles

It is known that substrate is the important part in the conventional CVD method, and the choice of substrate is essential to the morphology, nanostructure, and applications for carbonaceous nanomaterials. We generally use single transition metal substrate (Fe, Co, Ni, Cu, palladium (Pd) [41], ruthenium (Ru) [54]) as the catalyst for the preparation of graphene, and Fe, Co, Ni, and Cu are of great interest, because of the low cost and availability.

Remarkably, to build the uniform 3D architecture, single metal substrate is not enough for the CVD growth process. Hence, substrate embedded with metal nanoparticles serves as the bifunctional catalyst to facilitate the synthesis of different dimensional carbon materials, and the crucial issue for the in situ growth of 3D hybrids depends on the stability of catalyst nanoparticles during the deposition process. In CVD methods, the metal nanoparticles for the growth of hybrids could be obtained by a variety of ways, such as spin coating [47], electron evaporation [50], template etching [55, 56], and so on. Moreover, the covalent C–C bonding between different dimensional carbon materials, which is of paramount importance for 3D nanostructure, is probable to be achieved by such methods [57–59]. Nguyen et al. fabricated graphene/carbon nanotube composite by employing the Cu substrate-embedded Fe nanoparticles as the catalyst in the simple CVD approach [15]. In which Cu foil served as the template for the graphene sheet preparation. Additionally iron nanoparticles served as the catalyst for the CNT preparation. Besides, similar report indicated that the diameter, density, and quality of CNTs of composite could be defined by the size of the catalyst nanoparticles [45]. And various densities of catalyst nanoparticles had a different effect on the purity, thermal stability, and defects of 3D carbon hybrids [59].

#### 3.2 Effect of growth temperature

Although low-dimensional carbon nanomaterials' nanostructure and diameter in 3D architecture is directly related to the size and nature of catalyst nanoparticles, it also could be indirectly determined by adjusting growth temperature in CVD technique. The different growth of CNF/CNT hybrid was fabricated due to the different carbon source decomposition and diffusion rate at various growth temperatures in the study of Park et al. [24]. Furthermore, the growth temperature is also crucial for the defects and properties of 3D carbon nanomaterials. Lin et al. [57] found that at different growing temperatures, the various architecture of sample could be produced by indirectly changing the number of layers of graphene and packing density of CNTs. And the ratio of the  $I_D/I_G$  (Raman spectroscopy analysis), defects, and surface area increased with the decrease of growth temperature, leading to the increased specific capacitance. As a result, it is crucial to seek the appropriate growth temperature for the growth of well-developed 3D composite.

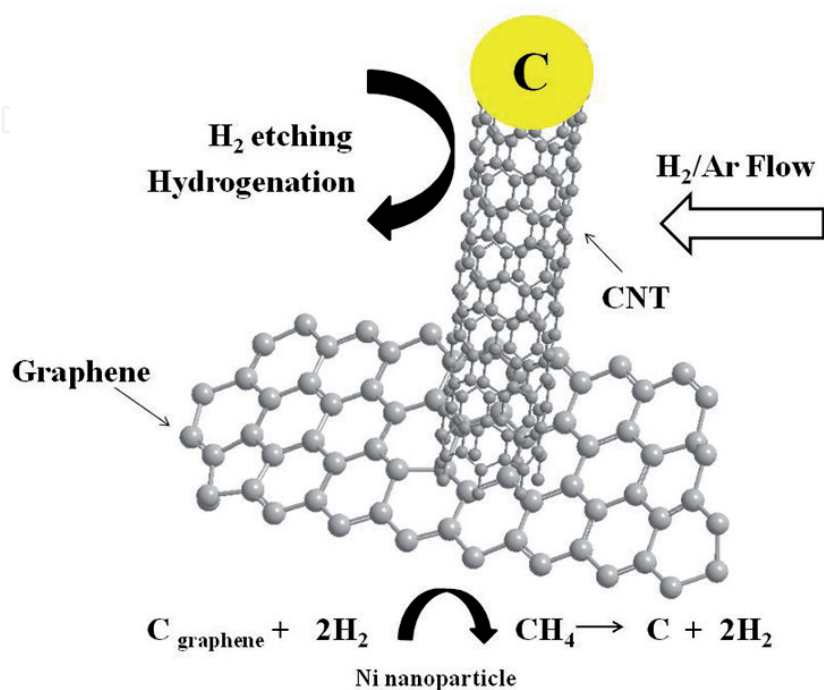
#### 3.3 Effect of carrier gas

In the CVD approach, hydrogen ( $H_2$ ), argon (Ar), and nitrogen ( $N_2$ ) are utilized for the growth of carbon materials in the high-temperature annealing process, and

the influence of variety of gases in the conventional CVD process is different. As for Ar and N<sub>2</sub>, they serve as the carrier gas to introduce the vapor into the CVD furnace under a suitable flow rate. As for H<sub>2</sub>, it has multifunctional effects in the practical CVD environment. First, it is believed that H<sub>2</sub> removes surface impurities (such as S and P) and defects which can cause local variations of carbon solubility in the metal substrate in the high-temperature process [13, 60]. And it also enables the reduction process of metal oxides for producing enough catalyst nanoparticles at the high temperature [10, 22, 24]. Yan et al. [49] fabricated mesoscopic 3D composite comprised of graphene and CNTs under the effect of Ni-Co catalysts which was produced at 800°C in H<sub>2</sub> atmosphere. Unlike the conventional CVD synthesis of individual 1D or 2D carbon nanostructure, H<sub>2</sub> also plays an important role in building nanostructure of 3D hierarchical hybrids, especially for graphene/CNT composite. For example, there were two simultaneous reactions appearing during the construction of 3D graphene/CNT hybrids in the previous report [8]. On one time, the methane decomposed with the increasing temperature and thereafter facilitates the CNT growth out of islands of metal catalyst. Simultaneously, hydrogenation process appeared on the surface of graphene sheet (shown in **Figure 6**). In this process, graphene sheet was effectively etched under the atmosphere of H<sub>2</sub> and transformed into CH<sub>4</sub> at the point of connection with the catalyst nanoparticles (Ni nanoparticle + C graphene + 2H<sub>2</sub> → Ni + CH<sub>4</sub>) [61]. Furthermore, the morphology of the hybrids was adjusted via varying the H<sub>2</sub> flow rate to change the two contrary reactions in the CVD method. Consequently, the high density of CNTs grown on the surface of graphene sheet under the suitable flow rate of H<sub>2</sub>, implying that the rate of H<sub>2</sub> etching optimized the 3D nanocarbon formation.

### 3.4 Effect of carbon source

So far, quite a few investigations have been dedicated to the fabrication of 3D carbonaceous hybrids by using various carbon sources, and studies have illustrated that the carbon sources can also be basically classified into the three categories: hydrocarbon compounds (CH<sub>4</sub> [45, 58], C<sub>2</sub>H<sub>2</sub> [11, 50], C<sub>2</sub>H<sub>4</sub> [10], C<sub>3</sub>H<sub>8</sub> [43]), liquid



**Figure 6.**  
 Schematics illustrating direct CNT growth on planar graphene under H<sub>2</sub> etching.



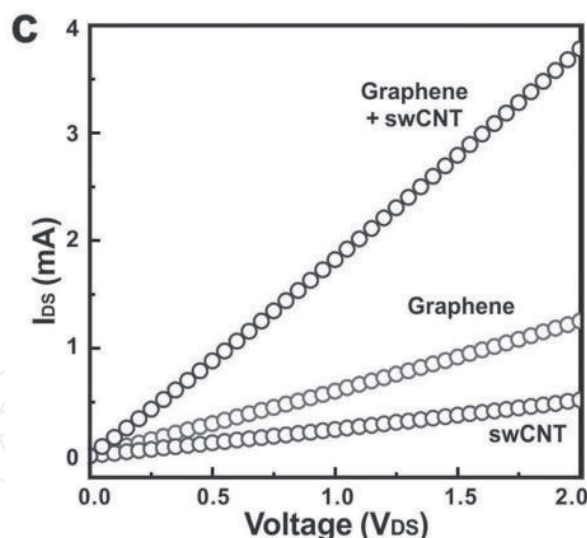
carbon sources (ethanol [47], pyridine [22], toluene [41]), and solid feedstock (melamine [49], Prussian blue [9], camphor [62]) and so on. According to the relevant reports, diverse carbonaceous hybrids choose various carbon sources as feedstock for the basic supply of 3D architecture. With respect to CNT/CNF hybrids, hydrocarbon compounds are always considered as feedstocks of CNTs on the surface of obtained CNFs. With respect to CNT/graphene or CNF/graphene composites, hydrocarbon compounds, liquid carbon sources, and solid feedstock are all used as precursors for the growth of hierarchical architecture. Notably, for the synthesis of graphene, the present CVD technique requires high growth temperature, typically 1000°C [63–65]. Since it is more environment-friendly, convenient, and economical for industrial fabrication, a low-temperature route is greatly desirable. Liquid and solid carbon sources decompose at a lower temperature relative to major gaseous carbon sources. Therefore, liquid and solid feedstock could be a better choice for the growth of 3D CNT/graphene or CNF/graphene hybrids because of the quick carbon diffusivity through metal catalysts and covering on the surface at lower temperature. Moreover, during the dehydrogenation process of liquid or solid carbon sources, the overall dehydrogenation barrier and nucleation barrier are much lower than that of gaseous carbon source from the relevant report [66]. Recently, low temperature (800°C) one-step CVD synthesis of 3D hybrids composed by CNTs and graphene sheet are demonstrated by using melamine as the single solid carbon source [56]. Nevertheless, 3D hybrid growth at lower temperature still remains a challenge.

#### 4. Development trend and application prospect of three-dimensional nanocarbon hybrids

Three-dimensional nanocarbon hybrids have been used for a variety of applications, for example, transparent and flexible electrodes and field-effect transistors [12–16, 47], sensors [17–20], fuel cell [67], batteries [9, 11, 44, 55], supercapacitors [10, 50, 51], and so on.

##### 4.1 Three-dimensional nanocarbon hybrids in transparent and flexible electrodes and field-effect transistors

Because of the outstanding mechanical, electrical, and thermal properties, low dimensional nanocarbon materials have recently attracted enormous interest for potential application in transparent and flexible nanoelectronics [68–70]. Furthermore, 3D graphene-based hybrids which offset shortcomings of pure graphene received a large number of attentions in particular for two applications: transparent and flexible electrodes and field-effect transistors. Kim et al. [13] successfully synthesized single-walled carbon nanotubes (SWCNT)/graphene hybrids on the Cu foil coated with CNTs. Notably, compared to pure CNT ( $58.78 \pm 36.17 \text{ cm}^2/\text{V s}$ ) and graphene ( $341.7 \pm 259.4 \text{ cm}^2/\text{V s}$ ), SWCNT-graphene hybrids possessed higher field-effect mobilities ( $\mu$ ) ( $394.46 \pm 176.27 \text{ cm}^2/\text{V s}$ ) and better output characteristics (**Figure 7**), suggesting that the electrical conductivity of this hybrids dramatically increased compared to individual carbon material. As for transparent and flexible device applications, the hybrids showed the low sheet resistance ( $300 \text{ }\Omega/\text{sq}$ ) with 96.4% optical transparency which is largely lower than the monolayer graphene ( $\sim 1 \text{ k}\Omega/\text{sq}$ ) grown by CVD method, indicating that composite is a promising material in developing high-performance transparent and flexible devices. Additionally, the hybrids possessed improved mechano-electrical property result from the CNT growth and obtained hybrid demonstrated that at an



**Figure 7.** Output characteristics ( $I_{DS} - V_{DS}$ ) of graphene, SWCNT-graphene hybrid film, and SWCNT. Reproduced with permission from ref. [13].

applied field of  $4.0 \text{ V}/\mu\text{m}$ , the hybrid exhibited a current density of  $1.33 \text{ mA cm}^{-2}$  [15], implying superiority than that of pure CNT materials on indium tin oxide films (ITO) glass [71]. And it probably replaces the ITO films, the most common transparent and flexible electrodes, as an alternative material with properties including high on/off ratios and outstanding electrical conductivity for high-performance flexible device in the future.

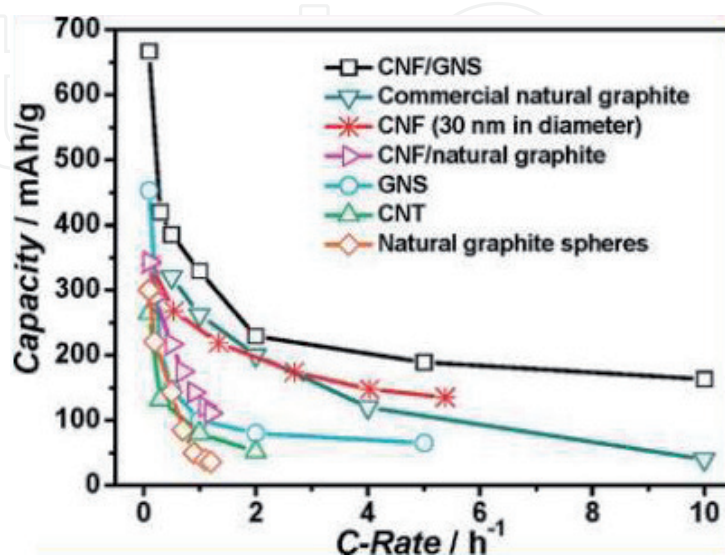
#### 4.2 Three-dimensional nanocarbon hybrids in fuel cell and batteries

In the practical application, the higher active and stable catalysts are crucial to the high electrochemical performance of fuel cell. Compared to the pure Pt-graphene cathode material, the Pt-3D nanocarbon composite cathode exhibits much smaller oxygen reduction reaction (ORR) charge transfer resistance and higher maximum power density in the direct methanol fuel cell [23] and proton exchange membrane fuel cells [21]. Moreover, due to the expensive cost and poor durability, as the spread anode and cathode electro-catalysts for ORR, Pt-based materials are hampered in the commercialization. Significantly, the CNT/CNF composite acts as the effective Pt-free ORR catalyst with a comparable activity, cheap price, and better thermal stability and durability, and the unique 3D network results in the enhanced electrochemical performance [22], implying 3D hybrid materials are becoming increasing competitive in the fuel cell applications.

Carbon-based materials (such as CNTs, CNFs, graphene), with their merits of reversible lithium-carbon reaction, low-intercalation potential with  $\text{Li}^+$ , high-coulombic efficiencies, and low-capacity fade, are excellent choices as electrode materials of lithium-ion batteries [72, 73]. Nevertheless, the cycling performance and high-rate capability of individual material are not as satisfactory as expected, possibly owing to the large contact resistance of easy self-aggregation and stacking. Moreover, hybrids consisting of various low dimensional carbon materials, which favor different oriented diffusion of the lithium ion and the 3D nanocarbon architecture, are beneficial to the electrons' collection and transport around the cycling process, leading to high electrical conductivity and chemical stability. For example, the 3D nanocarbon hybrid anode exhibited significantly enhanced reversible capacity ( $300 \text{ mA h g}^{-1}$ ), outstanding cycling stability, and lower electrolyte resistance and contact resistances in contrast with the individual CNF material [11].

Additionally, by building 3D carbon network, at current densities of 0.36, 0.6, 1.2, 2.4, and 6 mA/cm<sup>2</sup>, the rate performance of graphene/CNF hybrids reached about 420, 385, 329, 229, and 189 mA h g<sup>-1</sup>, (as shown in **Figure 8**), which were superior to those of other pure nanocarbon performances [44]. Therefore, hybridization of the different low-dimensional carbon nanomaterials is an effective route to provide fast ion/electron transfer and higher Li storage capability, and the hierarchical 3D carbonaceous architecture is also promising for Li-ion battery applications in the future.

Because of the large energy density, capacity (1673 mA h g<sup>-1</sup>), low cost, and environmental benignity of sulfur, lithium-sulfur (Li-S) batteries are investigated by a large number of research groups. However, the “shuttling effect” which always triggers an inevitable sulfur loss in practical Li-S battery applications, leading to an increase in internal resistance, low cycling capacity, and poor coulombic efficiency. To solve this problem, porous carbon materials, e.g., CNTs and graphene, also have been utilized to capture and encapsulate sulfur, blocking the high solubility of polysulfides during the Li-S battery applications [74, 75]. And compared to pure CNT which is always hindered by problems of easy self-aggregation, enormous interface resistance, and poor S-storage ability, the 3D hybrids composed of CNTs and graphene are more suitable for the cathode of high-rate performance for Li-S batteries. The hybrid structure exhibits unique advantages: (i) the well-connected junction between the CNTs and graphene sheets enable rapid electron transfer; (ii) robust nanostructure provides flexibility and mechanical robustness, which effectively buffers volume changes during the cycling process [9]. Zhao et al. reported that graphene/CNT composite cathode possessed remarkable performance: a reversible capacity (928 mA h g<sup>-1</sup>) at 1 C capacity and at a high current rate of 5 C, the capacity as high as about 650 mA h g<sup>-1</sup> could be obtained even after 100 cycles with a coulombic efficiency of about 92% in Li-S battery applications [76]. Furthermore, it is worth noting that electrochemical performance and catalytic activity have significantly improved nitrogen doping according to a relevant report, thus nitrogen-doped 3D hybrids also applied in the Li-S batteries. Tang et al. employed glucose and dicyandiamide as the carbon and nitrogen feedstocks to prepare the nitrogen-doped nanocarbon hybrid by a one-step chemical vapor deposition process technique, and the result (1314 mA h g<sup>-1</sup> at 0.2 C, a capacity retention



**Figure 8.** Comparison of the rate capabilities of CNF/GNS, GNS, CNT, commercial natural graphite discharged at C/5, CNF (30 nm in diameter), CNF/natural graphite, and natural graphite spheres. Reproduced with permission from ref. [44].

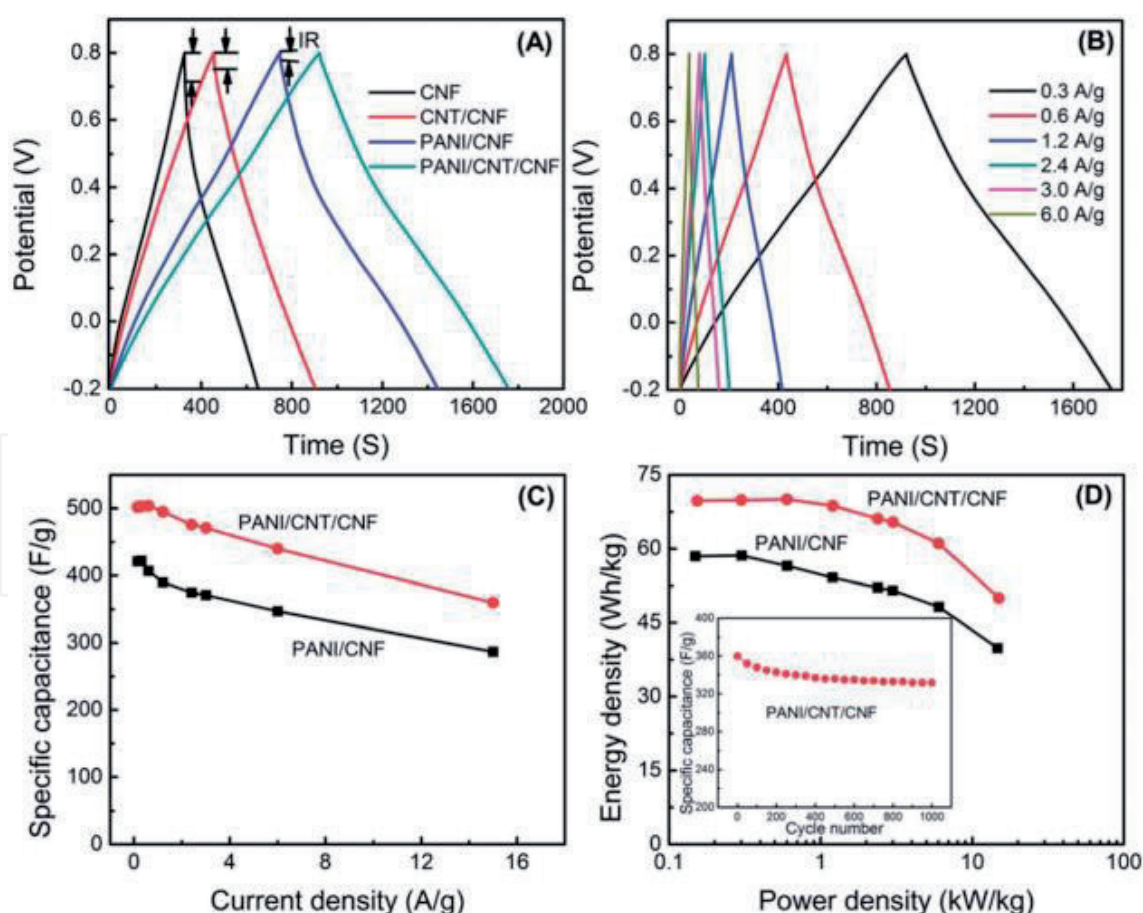


of 97% after 200 cycles at a high rate of 2 C) exhibited the improved cyclic and rate performances [9]. These experimental results also indicate that the nitrogen-doped 3D nanostructure has the potential toward promising Li-S batteries.

### 4.3 Three-dimensional nanocarbon hybrids in supercapacitors

A variety of nanocarbon materials, e.g., CNTs, graphene, or mesoporous and activated carbon possess enormous specific surface areas yet are limited by low performance owing to aggregation and internal resistance, leading to decreased capacitance than theoretical prediction [77]. To overcome the aforementioned disadvantages, 3D composites are considered as attractive materials for supercapacitor application by inhibiting the agglomeration and improving the electrolyte electrode accessibility and the electrode conductivity. Relevant report demonstrated that the capacitance ( $653.7 \mu\text{F cm}^{-2}$ ) at  $10 \text{ mV s}^{-1}$  of 3D CNT/graphene-based supercapacitor was superior to the graphene electrode ( $99.6 \mu\text{F cm}^{-2}$ ) [8]. Zhou et al. fabricated supercapacitor based on polyaniline/carbon nanotube/carbon nanofiber (PANI/CNT/CNF) electrode [30]. Compared with pure PANI/CNF, the hybrids showed higher specific capacitance and energy density, superior rate capability, and lower ion diffusion/transport resistance (shown in Figure 9).

Meanwhile, due to the merits—high theoretical capacity, low cost, and natural abundance—diverse potential metal oxides, e.g.,  $\text{RuO}_2$  [78],  $\text{MnO}_2$  [79],  $\text{NiO}$  [80],



**Figure 9.** (A) GCD curves of CNF, CNT/CNF, PANI/CNF, and PANI/CNT/CNF film electrodes at a current density of  $0.3 \text{ A g}^{-1}$ , respectively. (B) GCD curves of PANI/CNT/CNF film electrodes at different current densities. (C) Specific capacitance vs. current density for PANI/CNF and PANI/CNT/CNF film electrodes. (D) Charging/discharging cycling stability of PANI/CNT/CNF film electrodes at a current density of  $15 \text{ A g}^{-1}$ . Reproduced with permission from ref. [30].



and  $\text{Co}_3\text{O}_4$  [81] are regarded as the potential materials for pseudocapacitors. Particularly, as one of the most promising pseudocapacitor materials, when the  $\text{MnO}_2$  combined with 3D carbon hybrid, the drawbacks such as weak conductivity, low specific surface area, and brittleness of metal oxide electrodes are effectively alleviated, resulting in higher electrochemical performances [26, 27]. Wang et al. synthesized nanocarbon hierarchical composites (CNTs/CNFs) decorated with  $\text{MnO}_2$  for flexible supercapacitors [10]. And the 3D nanocarbon hybrid/ $\text{MnO}_2$  electrodes showed large better specific capacitance, cycling stability, maximum energy density, and rate capability than the CNF/ $\text{MnO}_2$  electrodes. These enhanced electrochemical performances of hybridized-based electrodes indicate that the designed hierarchical structures of composites support a large special surface area for the reaction between electrolyte ions and metal oxides. Simultaneously, the special 3D nanostructures improve the electrode nanomaterials' electronic conductivity and facilitate transport channels for electrolyte ions. It is no doubt that 3D nanocarbon hybrids will have a crucial impact on the emerging materials of high-performance supercapacitor applications.

## 5. Conclusion and further prospects

To combine the merits of each building block, 3D nanocarbon structures (CNT/graphene, CNF/graphene, CNT/CNF hybrids) have been prepared by a variety of methods. The synthesis procedure, merits, and demerits of different approaches reported in the literatures are discussed in this chapter. Among them, chemical vapor deposition is regarded as the most promising fabrication method, and nicely hybrid architectures are achievable by this way. Nevertheless, there are various drawbacks and challenges in the practice synthesis. One of the great challenges in the CVD synthesis of the three-dimensional nanocarbon hybrids is convenience or simpleness when compared to preparation methods of individual nanocarbon materials. A simple scalable CVD method to fabricate controllable architecture of 3D nanocarbon hybrid is still crucial to industrial production. Furthermore, a variety of applications have been presented in this chapter. Compared to individual nanocarbon components, the superior performances of 3D nanocarbon hybrids signify their promising and wide application in the future, and 3D hybrid electrode materials are becoming more competitive in energy storage applications. It is worth mentioning that studies on the growth mechanism of 3D nanostructure which is necessary for the full understanding of CVD growth process is seldom reported from the relevant literatures. And some crucial problem still remained to be solved, particularly the interactions between various individual components and structure control in the future.

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## References

- [1] Baughman RH, Zakhidov AA, de Heer WA. Carbon nanotubes-the route toward applications. *Science*. 2002;**297**(5582):787-792
- [2] Ebbesen TW, Ajayan PM. Large-scale synthesis of carbon nanotubes. *Nature*. 1992;**358**(6383):220-222
- [3] De Arco LG, Zhang Y, Kumar A, Zhou CW. Synthesis, transfer, and devices of single-and few-layer graphene by chemical vapor deposition. *IEEE Transactions on Nanotechnology*. 2009;**8**(2):135-138
- [4] Hammel E, Tang X, Trampert M, Schmitt T, Mauthner K, Eder A, et al. Carbon nanofibers for composite applications. *Carbon*. 2004;**42**(5-6):1153-1158
- [5] Huang X, Zeng ZY, Fan ZX, Liu JQ, Zhang H. Graphene-based electrodes. *Advanced Materials*. 2012;**24**(45):5979-6004
- [6] Novoselov KS, Geim AK, Morozov SV, Jiang D, Katsnelson MI, Grigorieva IV, et al. Two-dimensional gas of massless Dirac fermions in graphene. *Nature*. 2005;**438**:197-200
- [7] Xia XH, Chao DL, Fan ZX, Guan C, Cao XH, Zhang H, et al. A new type of porous graphite foams and their integrated composites with oxide/polymer core/shell nanowires for supercapacitors: Structural design, fabrication, and full supercapacitor demonstrations. *Nano Letters*. 2014;**14**(3):1651-1658
- [8] Kim YS, Kumar K, Fisher FT, Yang EH. Out-of-plane growth of CNTs on graphene for supercapacitor applications. *Nanotechnology*. 2012;**23**:15301-15307
- [9] Su DW, Cortie M, Wang GX. Fabrication of N-doped graphene-carbon nanotube hybrids from prussian blue for lithium-sulfur batteries. *Advanced Energy Materials*. 2017;**7**:1602014
- [10] Wang T, Song DF, Zhao H, Chen JY, Zhao CH, Chen LL, et al. Facilitated transport channels in carbon nanotube/carbon nanofiber hierarchical composites decorated with manganese dioxide for flexible supercapacitors. *Journal of Power Sources*. 2015;**274**:709-717
- [11] Kim H, Huang XK, Guo XR, Wen ZH, Cui SM, Chen JH. Novel hybrid carbon nanofiber/highly branched graphene nanosheet for anode materials in lithium-ion batteries. *ACS Applied Materials & Interfaces*. 2014;**6**:18590-18596
- [12] Li B, Cao XH, Ong HG, Cheah JW, Zhou XZ, Yin ZY, et al. All-carbon electronic devices fabricated by directly grown single-walled carbon nanotubes on reduced graphene oxide electrodes. *Advanced Materials*. 2010;**22**(28):3058-3061
- [13] Kim SH, Song W, Jung MW, Kang MA, Kim K, Chang SJ, et al. Carbon nanotube and graphene hybrid thin film for transparent electrodes and field effect transistors. *Advanced Materials*. 2014;**26**(25):4247-4252
- [14] Deng JH, Cheng GA, Zheng RT, Yu B, Li GZ, Hou XG, et al. Catalyst-free, self-assembly, and controllable synthesis of graphene flake-carbon nanotube composites for high-performance field emission. *Carbon*. 2014;**67**:525-533
- [15] Nguyen DD, Tai NH, Chen SY, Chueh YL. Controlled growth of carbon nanotube-graphene hybrid materials for flexible and transparent conductors and electron field emitters. *Nanoscale*. 2012;**4**(2):632-638

- [16] Hong TK, Lee DW, Choi HJ, Shin HS, Kim BS. Transparent. Flexible conducting hybrid multilayer thin films of multi-walled carbon nanotubes with Graphene Nanosheets. *ACS Nano*. 2010;**4**(7):3861-3868
- [17] Yan T, Wang Z, Wang YQ, Pan ZJ. Carbon/graphene composite nanofiber yarns for highly sensitive strain sensors. *Materials & Design*. 2018;**143**:214-223
- [18] Unnikrishnan B, Mani V, Chen SM. Highly sensitive amperometric sensor for carbamazepine determination based on electrochemically reduced graphene oxide–single-walled carbon nanotube composite film. *Sensors and Actuators B: Chemical*. 2012;**173**:274-280
- [19] Mani V, Devadas B, Chen SM. Direct electrochemistry of glucose oxidase at electrochemically reduced graphene oxide-multiwalled carbon nanotubes hybrid material modified electrode for glucose biosensor. *Biosensors and Bioelectronics*. 2013;**41**:309-315
- [20] Chen X, Zhu J, Xi Q, Yang W. A high performance electrochemical sensor for acetaminophen based on single-walled carbon nanotube–graphene nanosheet hybrid films. *Sensors and Actuators B: Chemical*. 2010;**161**(1):648-654
- [21] Yun YS, Kim D, Tak Y, Jin HJ. Porous graphene/carbon nanotube composite cathode for proton exchange membrane fuel cell. *Synthetic Metals*. 2010;**161**(21-22):2460-2465
- [22] Guo QH, Zhao D, Liu SW, Chen SL, Hanif M, Hou HQ. Free-standing nitrogen-doped carbon nanotubes at electrospun carbon nanofibers composite as an efficient electrocatalyst for oxygen reduction. *Electrochimica Acta*. 2014;**138**:318-324
- [23] Jha N, Jafri RI, Rajalakshmi N, Ramaprabhu S. Graphene-multi walled carbon nanotube hybrid electrocatalyst support material for direct methanol fuel cell. *International Journal of Hydrogen Energy*. 2011;**36**(12):7284-7290
- [24] Park M, Jung YJ, Kim JY, Lee HI, Cho J. Synergistic effect of carbon nanofiber/nanotube composite catalyst on carbon felt electrode for high-performance all-vanadium redox flow battery. *Nano Letters*. 2013;**13**:4833-4839
- [25] Dufficy MK, Khan SA, Fedkiw PS. Hierarchical graphene-containing carbon nanofibers for lithium-ion battery anodes. *ACS Applied Materials & Interfaces*. 2016;**8**(2):1327-1336
- [26] Xiong CY, Li TH, Dang A, Zhao TK, Li H, Lv HQ. Two-step approach of fabrication of three-dimensional MnO<sub>2</sub> graphene-carbon nanotube hybrid as a binder-free supercapacitor electrode. *Journal of Power Sources*. 2016;**306**:602-610
- [27] Lee DG, Kim BH. MnO<sub>2</sub> decorated on electrospun carbon nanofiber/graphene composites as supercapacitor electrode materials. *Synthetic Metals*. 2016;**219**:115-123
- [28] Fan ZJ, Yan J, Zhi LJ, Zhang Q, Wei T, Feng J, et al. A three-dimensional carbon nanotube/graphene sandwich and its application as electrode in supercapacitors. *Advanced Materials*. 2010;**22**:3723-3728
- [29] Zhao L, Qiu YJ, Yu J, Deng XY, Dai CL, Bai XD. Carbon nanofibers with radially grown graphene sheets derived from electrospinning for aqueous supercapacitors with high working voltage and energy density. *Nanoscale*. 2013;**5**:4902-4909
- [30] Zhou ZP, Wu XF, Hou HQ. Electrospun carbon nanofibers surface-grown with carbon nanotubes and polyaniline for use as high-performance electrode materials of supercapacitors. *RSC Advances*. 2014;**4**(45):23622-23629



- [31] Tung VC, Chen LM, Allen MJ, Wassei JK, Nelson K, Kaner RB, et al. Low-temperature solution processing of graphene-carbon nanotube hybrid materials for high-performance transparent conductors. *Nano Letters*. 2009;**9**(5):1949-1955
- [32] King PJ, Khan U, Lotya M, De S, Coleman JN. Improvement of transparent conducting nanotube films by addition of small quantities of graphene. *ACS Nano*. 2010;**4**(7):4238-4246
- [33] Tang Y, Gou J. Synergistic effect on electrical conductivity of few-layer graphene/multi-walled carbon nanotube paper. *Materials Letters*. 2010;**64**(22):2513-2516
- [34] Khan U, O'Connor I, Gun'ko YK, Coleman JN. The preparation of hybrid films of carbon nanotubes and nano-graphite/graphene with excellent mechanical and electrical properties. *Carbon*. 2010;**48**(10):2825-2830
- [35] Hong TK, Lee DW, Choi HJ, Shin HS, Kim BS. Transparent, flexible conducting hybrid multilayer thin films of multiwalled carbon nanotubes with graphene nanosheets. *ACS Nano*. 2010;**4**(7):3861-3868
- [36] Kim YK, Min DH. Durable large-area thin films of graphene/carbon nanotube double layers as a transparent electrode. *Langmuir*. 2009;**25**(19):11302-11306
- [37] Chen P, Xiao TY, Qian YH, Li SS, Yu SH. A nitrogen-doped graphene/carbon nanotube nanocomposite with synergistically enhanced electrochemical activity. *Advanced Materials*. 2013;**25**(23):3192-3196
- [38] Gong QM, Li Z, Zhou XW, Wu JJ, Wang Y, Liang J. Synthesis and characterization of in situ grown carbon nanofiber/nanotube reinforced carbon/carbon composites. *Carbon*. 2005;**43**(11):2426-2429
- [39] Thostenson ET, Li WZ, Wang DZ, Ren ZF, Chou TW. Carbon nanotube/carbon fiber hybrid multiscale composites. *Journal of Applied Physics*. 2002;**91**(9):6034-6037
- [40] Gaikwad AV, Rout TK, Van der Plas D, Dennis RV, Banerjee S, Pacheco Benito S, et al. Carbon nanotube/carbon nanofiber growth from industrial by-product gases on low- and high-alloy steels. *Carbon*. 2012;**50**(12):4722-4731
- [41] Lai C, Guo Q, Wu XF, Reneker DH, Hou H. Growth of carbon nanostructures on carbonized electrospun nanofibers with palladium nanoparticles. *Nanotechnology*. 2008;**19**(19):195303
- [42] Feng JM, Dai YJ. Water-assisted growth of graphene on carbon nanotubes by the chemical vapor deposition method. *Nanoscale*. 2013;**5**(10):4422-4426
- [43] Sahoo RK, Jeyapandiarajan P, Devi Chandrasekhar K, Daniel BSS, Venimadhav A, Sant SB, et al. Single-step synthesis of graphene-carbon nanofiber hybrid material and its synergistic magnetic behaviour. *Journal of Alloys and Compounds*. 2014;**615**:348-354
- [44] Fan ZJ, Yan J, Wei T, Ning GQ, Zhi LJ, Liu JC, et al. Nanographene-constructed carbon nanofibers grown on graphene sheets by chemical vapor deposition: High-performance anode materials for lithium ion batteries. *ACS Nano*. 2011;**5**(4):2787-2794
- [45] Van Chuc N, Thanh CT, Van Tu N, Phuong VTQ, Thang PV, Thanh Tam NT. A simple approach to the fabrication of graphene-carbon nanotube hybrid films on copper substrate by chemical vapor deposition.

Journal of Materials Science and Technology. 2015;**31**(5):479-483

[46] Lee DH, Kim JE, Han TH, Hwang JW, Jeon S, Choi SY, et al. Versatile carbon hybrid films composed of vertical carbon nanotubes grown on mechanically compliant graphene films. *Advanced Materials*. 2010;**22**(11):1247-1252

[47] Dong XC, Li B, Wei A, Cao XH, Chan-Park MB, Zhang H, et al. One-step growth of graphene-carbon nanotube hybrid materials by chemical vapor deposition. *Carbon*. 2011;**49**(9):2944-2949

[48] Su Q, Liang Y, Feng X, Müllen K. Towards free-standing graphene/carbon nanotube composite films via acetylene-assisted thermolysis of organocobalt functionalized graphene sheets. *Chemical Communications*. 2010;**46**(43):8279-8281

[49] Yan XL, Li HF, Wang C, Jiang BB, Hu HY, Xie N, et al. Melamine as a single source for fabrication of mesoscopic 3D composites of N-doped carbon nanotubes on graphene. *RSC Advances*. 2018;**8**(22):12157-12164

[50] Zhu Y, Li L, Zhang CG, Casillas G, Sun ZZ, Yan Z, et al. A seamless three-dimensional carbon nanotube graphene hybrid material. *Nature Communications*. 2012;**3**(1):1225

[51] Yu DS, Dai LM. Self-assembled graphene/carbon nanotube hybrid films for supercapacitors. *The Journal of Physical Chemistry Letters*. 2010;**1**(2):467-470

[52] Sakthinathan S, Kubendhiran S, Chen SM. Hydrothermal synthesis of three dimensional graphene-multiwalled carbon nanotube nanocomposite for enhanced electro catalytic oxidation of caffeic acid. *Electroanalysis*. 2016;**29**(4):1103-1112

[53] Tang C, Zhang Q, Zhao MQ, Tian GL, Wei F. Resilient aligned carbon nanotube/graphene sandwiches for robust mechanical energy storage. *Nano Energy*. 2014;**7**:161-169

[54] Mattevi C, Kim H, Chhowalla M. A review of chemical vapour deposition of graphene on copper. *Journal of Materials Chemistry*. 2011;**21**(10):3324-3334

[55] Ding YL, Kopold P, Hahn K, van Aken PA, Maier J, Yu Y. Facile solid-state growth of 3D well-interconnected nitrogen-rich carbon nanotube-graphene hybrid architectures for lithium-sulfur batteries. *Advanced Functional Materials*. 2016;**26**(7):1112-1119

[56] Li HF, Wu F, Wang C, Zhang PX, Hu HY, Xie N, et al. One-step chemical vapor deposition synthesis of 3D N-doped carbon nanotube/N-doped graphene hybrid material on nickel foam. *Nanomaterials*. 2018;**8**:700

[57] Lin CC, Lin YW. Synthesis of carbon nanotube/graphene composites by one-step chemical vapor deposition for electrodes of electrochemical capacitors. *Journal of Nanomaterials*. 2015;**2015**:1-8

[58] Zhang WL, Xie HH, Zhang RF, Jian MQ, Wang CY, Zheng QS, et al. Synthesis of three-dimensional carbon nanotube/graphene hybrid materials by a two-step chemical vapor deposition process. *Carbon*. 2015;**86**:358-362

[59] Zhao MQ, Peng HJ, Zhang Q, Huang JQ, Tian GL, Tang C, et al. Controllable bulk growth of few-layer graphene/single-walled carbon nanotube hybrids containing Fe@C nanoparticles in a fluidized bed reactor. *Carbon*. 2014;**67**:554-563

[60] Rummeli MH, Rocha CG, Ortmann F, Ibrahim I, Sevincli H, Börrnert F, et al. Graphene: Piecing it together. *Advanced Materials*. 2011;**23**(39):4471-4490

- [61] Ci LJ, Song L, Jariwala D, Elías AL, Gao W, Terrones M, et al. Graphene shape control by multistage cutting and transfer. *Advanced Materials*. 2009;**21**(44):4487-4491
- [62] Shinde SM, Kalita G, Sharma S, Papon R, Yusop MZ, Tanemura M. Synthesis of a three dimensional structure of vertically aligned carbon nanotubes and graphene from a single solid carbon source. *RSC Advances*. 2014;**4**(26):13355-13360
- [63] Li X et al. Large-area synthesis of high-quality and uniform graphene films on copper foils. *Science*. 2009;**324**(5932):1312-1314
- [64] Lee S, Lee K, Zhong ZH. Wafer scale homogeneous bilayer graphene films by chemical vapor deposition. *Nano Letters*. 2010;**10**(11):4702-4707
- [65] Li XS, Cai WW, Colombo L, Ruoff RS. Evolution of graphene growth on Ni and Cu by carbon isotope labeling. *Nano Letters*. 2009;**9**(12):4268-4272
- [66] Li ZC, Wu P, Wang CX, Fan XD, Zhang WH, Zhai XF, et al. Low-temperature growth of graphene by chemical vapor deposition using solid and liquid carbon sources. *ACS Nano*. 2011;**5**:3385-3390
- [67] Li SS, Luo YH, Lv W, Yu WJ, Wu S, Hou PX, et al. Vertically aligned carbon nanotubes grown on Graphene paper as electrodes in lithium-ion batteries and dye-sensitized solar cells. *Advanced Energy Materials*. 2011;**1**(4):486-490
- [68] Javey A, Guo J, Wang Q, Lundstrom M, Dai H. Ballistic carbon nanotube field-effect transistors. *Nature*. 2003;**424**(6949):654-657
- [69] Kakade BA, Pillai VK, Late DJ, Chavan PG, Sheini FJ, More MA, et al. High current density, low threshold field emission from functionalized carbon nanotube bucky paper. *Applied Physics Letters*. 2010;**97**(7):073102
- [70] Novoselov KS, Geim AK, Morozov SV, Jiang D, Zhang Y, Dubonos SV, et al. Electric field effect in atomically thin carbon films. *Science*. 2004;**306**(5696):666-669
- [71] Yang H, Shang X, Li Z, Qu S, Gu Z, Xu Y, et al. Synthesis of large-area single-walled carbon nanotube films on glass substrate and their field electron emission properties. *Materials Chemistry and Physics*. 2010;**124**(1):78-82
- [72] Obrovac MN, Christensen L. Structural changes in silicon anodes during lithium insertion/extraction. *Electrochemical and Solid-State Letters*. 2004;**7**(5):A93-A96
- [73] Winter M, Besenhard JO, Spahr ME, Novák P. Insertion electrode materials for rechargeable lithium batteries. *Advanced Materials*. 1998;**10**(10):725-763
- [74] Zhou G, Wang DW, Li F, Hou PX, Yin LC, Liu C, et al. A flexible nanostructured Sulphur-carbon nanotube cathode with high rate performance for Li-S batteries. *Energy & Environmental Science*. 2012;**5**(10):8901-8906
- [75] Wang HL, Yang Y, Liang YY, Robinson JT, Li YG, Jackson A, et al. Graphene-wrapped sulfur particles as a rechargeable lithium-sulfur battery cathode material with high capacity and cycling stability. *Nano Letters*. 2011;**11**(7):2644-2647
- [76] Zhao MQ, Liu XF, Zhang Q, Tian GL, Huang JQ, Zhu WC, et al. Graphene/single-walled carbon nanotube hybrids: One-step catalytic growth and applications for high-rate Li-S batteries. *ACS Nano*. 2012;**6**(12):10759-10769

[77] Zhang LL, Zhao XS. Carbon-based materials as supercapacitor electrodes. *Chemical Society Reviews*. 2009;**38**(9):2520-2531

[78] Wu ZS, Wang DW, Ren W, Zhao J, Zhou G, Li F, et al. Anchoring hydrous RuO<sub>2</sub> on graphene sheets for high-performance electrochemical capacitors. *Advanced Functional Materials*. 2010;**20**(20):3595-3602

[79] Lv P, Feng YY, Li Y, Feng W. Carbon fabric-aligned carbon nanotube/MnO<sub>2</sub>/conducting polymers ternary composite electrodes with high utilization and mass loading of MnO<sub>2</sub> for supercapacitors. *Journal of Power Sources*. 2012;**220**:160-168

[80] Liu J, Jiang J, Bosman M, Fan HJ. Three-dimensional tubular arrays of MnO<sub>2</sub>-NiO nanoflakes with high areal pseudocapacitance. *Journal of Materials Chemistry*. 2012;**22**(6):2419-2426

[81] Liu JP, Jiang J, Cheng CW, Li HX, Zhang JX, Gong H, et al. Co<sub>3</sub>O<sub>4</sub> nanowire@MnO<sub>2</sub> ultrathin nanosheet core/shell arrays: A new class of high-performance Pseudocapacitive materials. *Advanced Materials*. 2011;**23**(18):2076-2081