

Chapter 2

Strategies for the Hybridization of CNTs with Graphene

Abstract Graphene and CNTs have attracted tremendous attention and research interest owing to its exceptional physical properties such as high electronic conductivity, good thermal stability, and excellent mechanical strength. However, the agglomeration of carbon materials, specially, graphene and CNTs, are inevitable owing to the strong van der Waals forces between themselves. Hybridization of CNTs with graphene can not only prevent the aggregation of these carbon materials but also realize synergistic effect between graphene and CNTs. Studies have proved that graphene-CNT hybrid nanomaterials exhibit higher electrical conductivities, larger specific area, and better catalytic properties compared with either pristine CNTs or graphene. The structure of the hybrids is diverse and can be prepared by several approaches including simple solution assembly, chemical vapor deposition method, and unzipping of CNTs. In this chapter, strategies for the hybridization of CNTs with graphene and characterization of the hybrid are summarized and discussed.

Keywords Graphene • Carbon nanotubes • Hybridization • Solution assembly • Chemical vapor deposition • Unzipping

Graphene, with high specific area and conductivity, has great potential applications in many fields such as electronic devices, solar cells, sensors, supercapacitors, and hydrogen storage. However, the practical applications of graphene materials are severely restrained by the agglomeration of graphene sheets owing to their strong van der Waals interactions. Obviously, one of the best strategies to materialize the great potential of graphene for various applications is to add some spacer between the stacked graphene sheets to avoid such restacking and agglomerate formation, and in the meantime, the spacer could best contribute to the overall surface area and/or electrical conductivity of the whole materials [1]. As for the spacers, CNTs stand out as an ideal candidate because of their high conductivity, large specific surface, and most importantly, the intimate interaction with graphene sheets due to their similar carbon structure [2–5]. By bridging the graphene sheets, the CNTs can greatly reduce the internal electrical resistance and improve the overall electrical

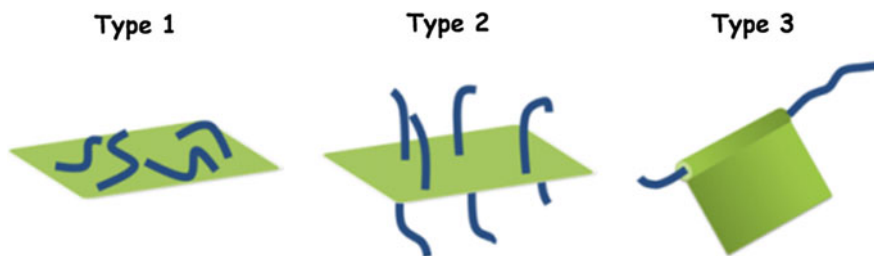


Fig. 2.1 Three types of the hybrids of graphene and CNTs

conductivity. Therefore, fabrication of graphene/CNT hybrids has brought extensive interest.

The hybridization of 1D CNTs and 2D graphene is able to form nanostructured hybrids with different topological architectures [6]. Thus, according to their different nanostructures, the hybrids of CNTs and graphene are classified into three types: CNTs adsorbed horizontally to the graphene surface, CNTs adsorbed perpendicularly to the graphene surface, and CNT wrapped with graphene, as illustrated in Fig. 2.1. For CNTs adsorbed horizontally to graphene surface, graphene functioned as a continuous sheet matrix for holding up the CNTs, which is the most common type of graphene-CNT hybrids. For CNTs adsorbed perpendicularly to graphene surface, it is likely that this form is attributed to a single interaction point between graphene sheet and CNTs, where CNTs connect with graphene sheets through the catalyst particles during the chemical vapor deposition (CVD) process. For CNTs wrapped with graphene nanosheets, the wrapping form of hybrids depends on the interaction between graphene sheets and CNTs, as well as the proportion of CNTs.

Hybridization of graphene oxide (GO) or functionalized graphene with CNTs is usually realized by two different methods. The assembly method simply co-assembles graphene and CNTs together, while the in situ method involves unzipping CNTs into CNT/GNR hybrids or growing CNTs on graphene sheets. Table 2.1 shows the summary of the hybridization of graphene sheets with pristine or functionalized CNTs in solvents, as reported in the literatures.

2.1 Assembly Method

Graphene and CNTs co-assemble through van der Waals forces or π - π interactions by their aromatic sp^2 nanostructure to form hierarchical hybrids. Highly oxygenated functional groups of GO sheets or functional groups of CNTs are used to realize electrostatic or covalent assembly.

Table 2.1 The hybridization of graphene with CNTs in solvents

Graphene	CNTs	Interaction	Architecture	Dispersion solvent	Weight ratio (G: CNT)	Refs.
GO	SWCNT	van der Waals interaction	Type 1	Water	–	[7]
GO	MWCNT	π – π stacking	Type 1	Water	>3	[8]
GO salt	SWCNT	van der Waals interaction	Type 1	Water	0.5–5	[9]
GNS	A-MWCNT	Ion-coordinated interaction	Type 1	Water	<0.25	[10]
Chitosan-grafted GNS	MWCNT	van der Waals interaction	Type 1	Water	1	[11]
GO–PPD	MWCNT	Covalent bonding	Type 1	NMP	–	[12]
GO	SWCNT	π – π stacking	Type 3	Water	2.5	[13]
GO	NH ₂ -MWCNT	Covalent bonding	Type 3	Water	40	[14]
GNS	SWCNT	–	Type 1	Hydrazine	0.2	[15]
GNS	A-MWCNT	π – π stacking	Type 1	Water	1	[16]
GO	MWCNT	π – π stacking	Type 1	Water	>2	[17]
SDBS–rGO	SWCNT	van der Waals interaction	Type 1	Water		[18]
GO	SWCNT	–	–	Water	0.5	[19]

G Graphene; *GNS* Graphene nanosheets; *rGO* Reduced graphene oxide; *A-MWCNT* Acid-treated MWCNT; *PPD* *p*-Phenylenediamine; *SDBS* Sodium dodecylbenzene sulfonate

2.1.1 Solution Processing

Owing to the π -conjugated aromatic domains in its basal plane, GO can interact with CNTs via strong π – π interaction. Liu et al. [8] reported a noncovalent strategy to utilize GO sheets for stabilizing aqueous dispersions of CNTs with high weight fraction. This facile approach only entails mixing GO sheets with CNTs and mild sonication for a certain time, which has paved the way for reducing the CNT breakage. As shown in Fig. 2.2, the MWCNT–GO composites prepared through mild sonication and centrifugation show good solubility in water, which is very stable at room temperature with no precipitation for weeks. It is reasonable to suppose that the π -conjugated multiple aromatic regions of GO sheets could interact with the sidewalls of MWCNTs through the π -stacking interaction, while the hydrophilic oxygen groups maintain the water solubility of MWCNT–GO complexes. Besides, the water-soluble and insoluble complexes can be acquired by adjusting the initial proportion of GO sheets to MWCNTs, which are significant for noncovalent approaches toward dispersing CNTs in water. As shown in Fig. 2.2e, GO sheet with many conjugated clusters is prone to interact with MWCNTs when the weight ratio of MWCNTs to GO sheets was 2:1, thus forming MWCNT-coated

exfoliated GO sheets (Fig. 2.2f). Severe agglomeration of MWCNT–GO complexes was seen (the inset picture in Fig. 2.2e), because the excessive MWCNTs and the tubule-twisted CNTs fixed on GO sheets may reduce the solubility of MWCNT–GO complexes. However, when the weight ratio of MWCNTs to GO sheets was 1:2 (Fig. 2.2g), the single GO sheet can still first interact with lots of MWCNTs. Stable suspensions of MWCNT–GO complexes were formed after the dynamic equilibrium process owing to the long-time sonication (the inset picture in Fig. 2.2g). A small amount of hair-like MWCNTs were randomly anchored on the surface of GO sheets (Fig. 2.2h), forming the hydrophilic MWCNT–GO complexes.

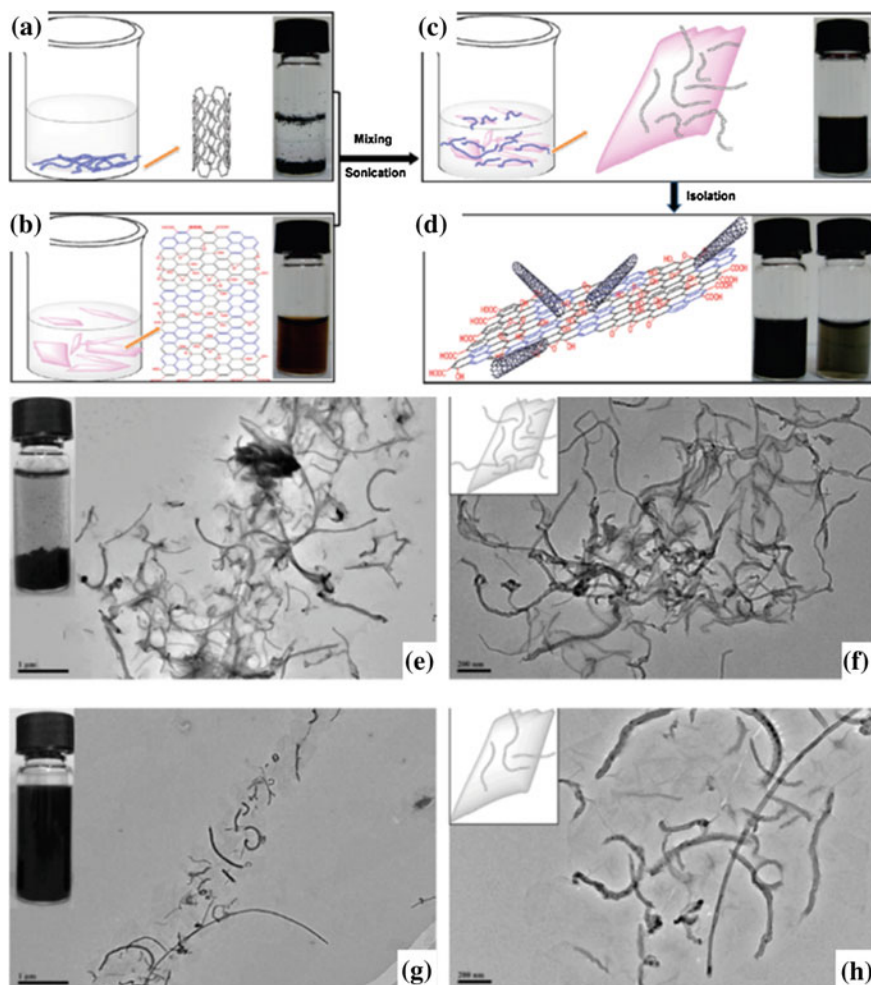


Fig. 2.2 a–d A schematic for the formation of the GO–MWCNT hybrids. TEM images of GO–MWCNT hybrids by adjusting the initial weight ratio of MWCNTs to GO sheets with 2:1 e, f and 1:2 g, h at low and high magnifications. Reprinted with the permission from Ref. [8]. Copyright 2010 American Chemical Society

Furthermore, the ability of GO sheets to stabilize the SWCNTs or MWCNTs with different outer diameters was further studied. It is found that the MWCNTs with diameters less than 8 nm cannot be dispersed by GO sheets. When the diameters of CNTs are less than a critical value, the surface energy between CNTs can compromise the π - π interactions, thus forming bundles or twisted structures of CNTs. This fact further indicates that the π -stacking interactions between the GO sheets and pristine MWCNTs induce such physical adsorption, and the π - π interactions are not strong enough to overcome the enhanced graphitic intertube interaction of the CNTs with diameters less than 8 nm. Interestingly, on the contrary, another work reported that GO sheets are highly effective in the dispersion of SWCNTs to form optically transparent solution-like aqueous suspensions [9]. As a demonstration for their valuable applications, the homogeneous dispersions were used for a more accurate determination of absorptivity for the band gap transitions in semiconducting SWCNTs. The use of aqueous GO-dispersed SWCNTs in the fabrication of transparent conductive coatings, though preliminary, has already achieved significant performance ($\sim 4 \text{ k}\Omega/\square$ for 85 % transmittance at 550 nm, with only simple air-spray fabrication).

Metal ion coordination is another effective way of interconnecting or “cross-linking” oxidized CNTs and GO by the oxygen-containing functional groups. Therefore, bonding CNTs and GO through the coordination chemistry is an effective way to fabricate graphene-CNT hybrids. Xie et al. [10] used divalent metal ions (M^{2+} , $M = \text{Cu, Ca or Mg}$) to realize coordination of GO sheets and oxidized MWCNTs through a facile, solution-based approach. Flexible and transparent conductive films of M^{2+} -coordinated CNT/GO networks are produced by spin coating. This approach paves a novel way for preparing transparent electrode materials with high flexibility and strength, showing great potential for development of biosensors and catalyst-loaded reactors.

Although GO can directly disperse CNTs in aqueous solution, the efficiency of GO to disperse CNTs is still limited because the basal plane of GO is not graphitic enough due to the epoxide and hydroxyl groups. It is reported that GO could hardly disperse and stabilize MWCNTs effectively if GO/MWCNT mass ratio was less than 1. Therefore, if we can make the basal plane of GO more graphitic by removing those oxygen-containing groups on basal planes of GO sheets, it should be able to disperse CNTs more efficiently. To make stable dispersions of reduced graphene oxide (rGO), it is necessary to functionalize GO with water-soluble polymers prior to the chemical reduction. These-polymer functionalized rGO sheets possess not only excellent solubility in water or other proper solvents but also fully graphitic basal planes. By taking advantage of the progress, it is possible to develop rGO derivatives with higher efficiency in dispersing and stabilizing CNTs. For instance, synergistic assembly of GO, SWCNTs, and conjugate polymer poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) in aqueous solution created an adhesive and conductive glue that was highly suitable as electrode in ultracapacitors [20]. Within the context of quasi-solid state electrolytes, Gun'Ko and coworkers [21] demonstrated that mixtures containing graphene, SWCNTs, and 1-methyl-3-propylimidazolium iodide (PMII) ionic liquid

(IL) displayed an increase in light conversion efficiencies not only as compared to pure PMIL, but also to the individual mixtures of PMII with either SWCNTs or graphene. The authors suggested that this significant increase occurred because of the efficient electron transfer in the IL-mediated self-organization of graphene and SWCNT nanomaterials. Li et al. [11] synthesized water-soluble chitosan-grafted reduced graphene oxide (CS-rGO) sheets via amidation reaction and chemical reduction. CS-rGO possesses not only remarkable graphitic property but also favorable water solubility, which is found to be able to effectively disperse MWCNTs in acidic solutions via noncovalent interaction. The efficiency of CS-rGO in dispersing MWCNTs is tested to be higher than that of plain GO and a commercial surfactant, sodium dodecyl sulfate. With incorporation of 1 wt% CS-rGO dispersed MWCNTs (CS-rGO-MWCNTs), the tensile modulus, strength, and toughness of the chitosan nanocomposites can be increased by 49, 114, and 193 %, respectively. Noncovalent π - π interactions between graphene sheets and nanotubes and hydrogen bonds between grafted CS and the CS matrix are responsible for generating effective load transfer between CS-rGO-MWCNTs and the CS matrix, causing the simultaneous increase in strength and toughness of the nanocomposites.

In addition to noncovalent π - π interactions, a novel chemical approach is established to design 3D MWCNT decorated rGO hybrid by the formation of covalent bonding between rGO and MWCNT without using any catalyst and surfactant [12]. Figure 2.3 illustrates the formation of chemically bonded rGO-MWCNT hybrid. Briefly, GO and *p*-phenylenediamine (PPD) were used as the precursors for the GO-PPD. The nucleophilic ring-opening reaction of epoxy group of GO by amine group of PPD could not only reduce and functionalize GO but also stitch it. The addition of NH_3 solutions rendered alkaline environment useful for the nucleophilic substitution reaction. This structure facilitates the formation of 3D hybrid network by diazotization of GO-PPD and sequential C-C coupling with MWCNTs via radical generation. Unlike the use of any catalyst or surfactant, the guest MWCNT was directly bonded to host GO-PPD by sp^2 carbons forming interconnected carbon structures of well-defined pores. Owing to the high conductance of GO-PPD, the fully accessible surface and extended conjugated network with well-defined pores, the obtained hybrid exhibits good electrical conductivity, attractive specific capacitance, excellent dye adsorption capacity for the application in supercapacitors, removal of dyes, and other electronic applications.

As mentioned above, the graphene-CNT hybrid can also be formed with graphene nanosheets wrapping on the surface of CNTs. Chen et al. [13] fabricated stable SWCNT aqueous suspension with SWCNTs wrapped by GO sheets to achieve core-shell nanostructures, which were formed when nanosized GO sheets were dispersed with CNTs whereas micron-sized GO sheets prefer adhesion of multiple CNTs onto the surface of a single GO sheet (Fig. 2.4a-c). This is the first time to experimentally demonstrate the spontaneous formation of SWCNT/GO nanoscrolls and its potential applications in optoelectronic devices and energy storage. Scrolled GOs (SGO) with MWCNT templates were prepared by Min et al. [14], and the synthesis strategies are shown in Fig. 2.4d. GO sheets were

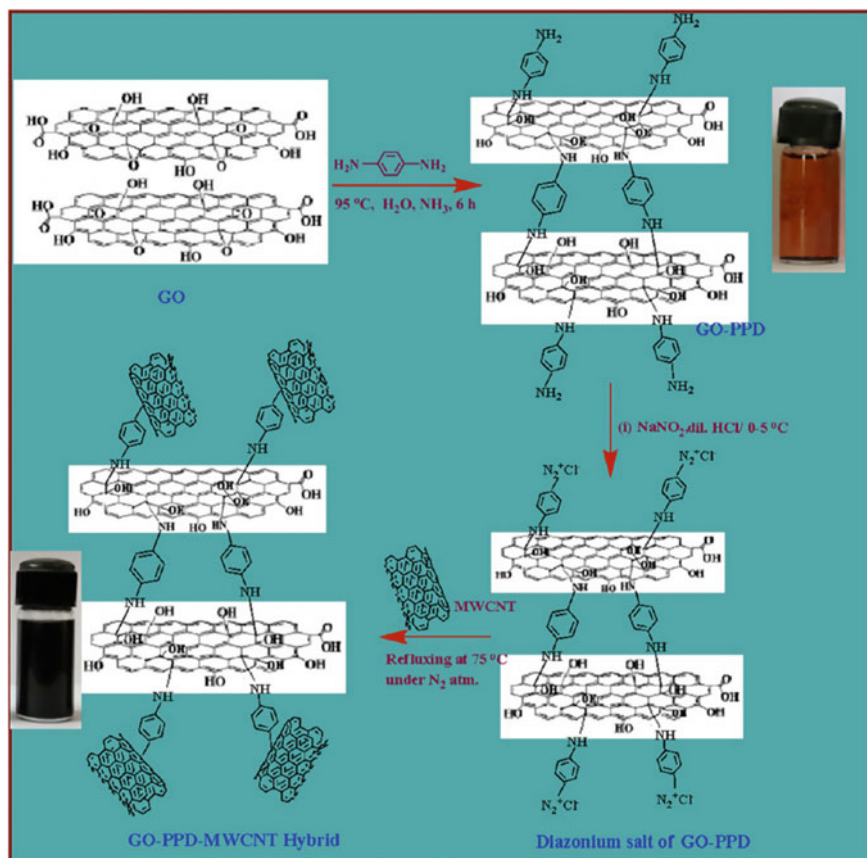


Fig. 2.3 A schematic for the formation of chemically bonded rGO–MWCNT hybrid. Reprinted with the permission from Ref. [12]. Copyright 2013 American Chemical Society

successfully made to adopt a scroll conformation around the surface of aminated MWCNT in solution by covalent bond formation, which would allow large-scale production of SGO/MWCNT hybrid materials.

Increasing the number of oxygenated groups enhances the dispersibility of GO sheets in water, but they also increase the defects in the sp^2 lattice structure and make GO sheets electrically insulating. Chemical and hydrothermal methods are used to reduce GO sheets while maintaining its conductivity. A conductive single layer of highly reduced graphene with evenly dispersed CNTs can be maintained when the reduction of GO happens after or during the assembly of GO–CNT hybrids. Stable dispersion of rGO–CNT hybrid was achieved through dispersing GO powder and oxidized CNTs in anhydrous hydrazine [15], which is more stable in aqueous than organic solvents. The rGO–CNT dispersions were readily deposited onto a variety of substrates by spin coating and subsequently heated to $150\text{ }^\circ\text{C}$ to remove excess

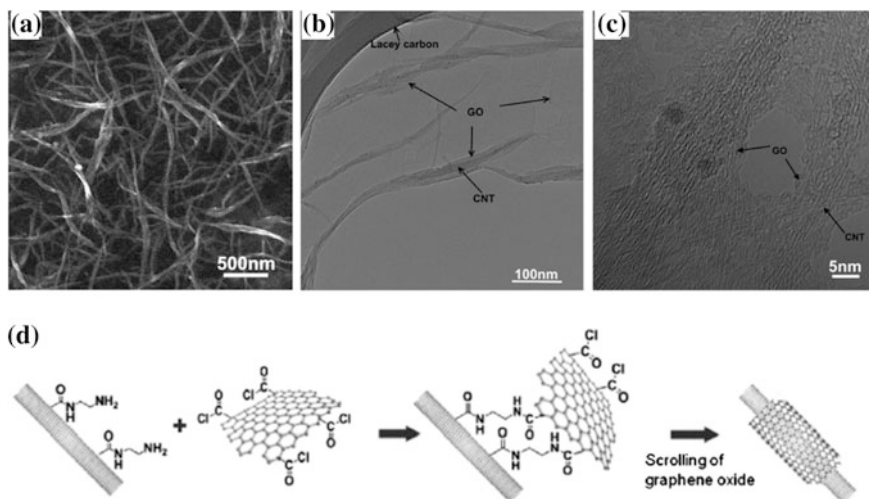


Fig. 2.4 **a** SEM image of SWCNT/GO, **b** TEM image, and **c** high-resolution TEM image of SWCNT/GO. Reprinted with the permission from Ref. [13]. Copyright 2011 Elsevier. **d** A scheme showing GO scroll formation around a MWCNT template by covalent conjugation. Reprinted with the permission from Ref. [14]. Copyright 2010 Elsevier

solvent. The film deposited at 1750 rpm showed optical transmittance of 92 % and a sheet resistance of only $636 \Omega/\square$. This sheet resistance is nearly two orders of magnitude lower than the analogous vapor-reduced GO films reported previously ($\sim 1 \text{ M}\Omega/\square$ and 80–85 % transmittance). The vast improvement in sheet resistance of a graphene–CNT electrode can be explained by the formation of an extended conjugated network with individual CNTs bridging the gaps between graphene sheets. The large graphene sheets cover the majority of the total surface area, while the CNTs act as wires connecting the large pads together.

Liu et al. [16] reported a facile approach to fabricate graphene–MWCNT hybrids through directly reducing GO sheets with acid-treated MWCNTs (A-MWCNTs) as shown in Fig. 2.5. Direct evidence for the hybridization of graphene with A-MWCNTs can be obtained by TEM observation (Fig. 2.5b–c). It can be clearly seen the rolled edge of the graphene which gives a folded appearance, and in some regions the well-separated A-MWCNTs were adsorbed on the graphene surface. Accompanied by A-MWCNTs assisted dispersion of rGO, the addition of rGO that acts as a CNT “carrier” assists in anchoring the CNTs on rGO nanosheets, thus achieving uniform codispersion for both CNTs and rGO in poly(vinyl alcohol) (PVA) matrices. Owing to the uniform dispersion and strong interaction of CNTs and rGO, the tensile strength and Young’s modulus of the final PVA composite with 0.6 wt% graphene–CNT hybrids are greatly enhanced by 77 and 65 %, respectively. This work paves a novel pathway for the synthesis of carbon hybrids for preparing high-performance polymer nanocomposites.

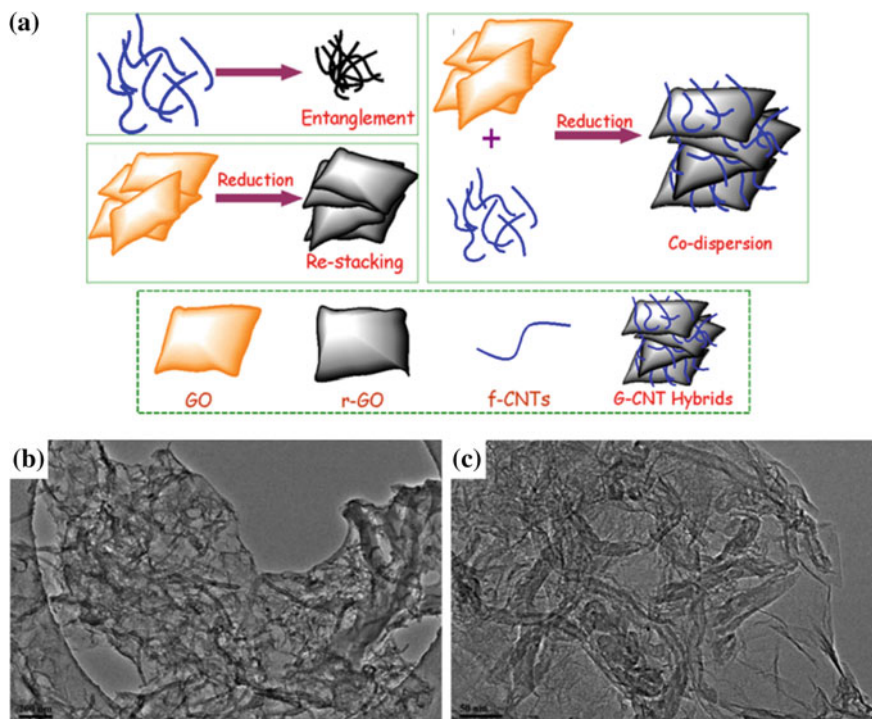


Fig. 2.5 a A schematic for the codispersion of rGO with the aid of A-MWCNTs. TEM images of rGO/A-MWCNT (1:1) hybrids at **b** low and **c** high magnifications. [Original citation]-Reprinted with the permission from Ref. [16]. Copyright 2012 Royal Society of Chemistry

2.1.2 Layer-by-Layer Assembly

Layer-by-layer (LBL) is a method to prepare thin films that is able to be controlled at nanometer scales. As a consequence, it is an effective method to fabricate graphene-CNT hybrid films [22–27]. Kim and Min reported a thin transparent MWCNTs–rGO hybrid film with double-layer structures [25]. The SiO₂/Si substrates were first coated with a layer of negatively charged rGO, and then coated with a layer of aminated MWCNTs. It was seen that the reaction between MWCNTs and rGO film greatly decreased the sheet resistance while maintaining its transparency and adhesion strength.

Hong et al. [26] presented a simple and novel strategy for creating multilayered thin films of highly conducting rGO nanosheets with MWCNTs via LBL assembly. A-MWCNTs with amino groups were obtained using excess ethylenediamine mediated *N*-ethyl-*N'*-(3-dimethylaminopropyl)carbodiimide methiodide chemistry.

Multilayer films of rGO/NH₂-MWCNT hybrids can be acquired by spin coating NH₂-MWCNT and rGO continuously on a substrate (Fig. 2.6). The integration of MWCNTs not only provides the electronic conductivity but also affords mechanical

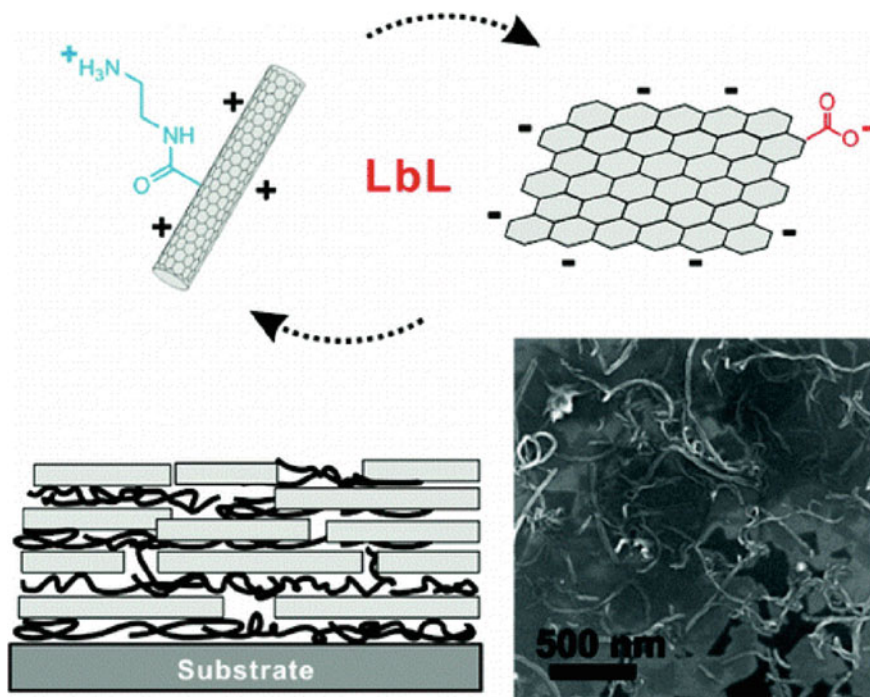


Fig. 2.6 A schematic representation of hybrid LbL multilayer of MWNTs and rGO, and SEM image of (MWNT/GO)₅ multilayer after chemical treatment with hydrazine. Reprinted with the permission from Ref. [26]. Copyright 2010 American Chemical Society

flexibility of the hybrid film, allowing the electronic contact of graphene nanosheets by bridging the gaps between graphene sheets. It was furthermore demonstrated that the assembled hybrid multilayer can be utilized as a flexible, transparent conducting electrode possessing high electrical conductivity and transparency while allowing significant flexibility.

Yu and Dai prepared thin film of MWCNTs–rGO hybrid through in situ reduction of GO sheets with the assistance of polymer-bound graphene nanosheets and cationic poly(ethyleneimine) [27]. This film can be deposited on a variety of other substrates, and the resulting films with carbon networks and nanopores can ensure fast ion diffusion, holding great potential for application in supercapacitors.

2.1.3 Vacuum Filtration

The bulky carbon materials show a variety of fascinating features that cannot be achieved from individual graphene sheet or carbon nanotubes. Vacuum filtration is employed to fabricate flexible graphene-CNT paper, which transforms nanoscale

building blocks into macroscopic architectures [28–31]. This new material outperforms many other paper-like materials in terms of stiffness and strength. Its combination of macroscopic flexibility and stiffness is a result of unique interlocking tile arrangement of the nanoscale graphene and CNTs.

Coleman et al. [32] developed a new approach to fabricate hybrid films (thickness from 10 to 100 μm) of SWCNTs and graphene/nanographite with various weight percentage of graphene/nanographite through vacuum filtration. Scanning electron microscopy shows the components to be well mixed with little sign of phase separation. Although dominated by nanographite, Raman spectroscopy shows the presence of some graphene flakes with less than five layers. Mechanical measurements show that the hybrids are stronger and stiffer than CNT- or graphene-only films, reaching strength and stiffness of 38 MPa and 4.8 GPa, respectively, for the sample with 20 wt% graphene. In addition, the hybrid films were more electrically conductive than the CNT- or graphitic-only films, reaching a conductivity of $2 \times 10^4 \text{ S m}^{-1}$ for the 70 wt% nanographite/graphene sample. Thin films of few-layer graphene (FLG) and MWCNTs fabricated by similar method were reported by Tang and Gou [33]. In the FLG/MWCNT paper, an entangled network of MWCNTs was formed to bridge the gap between FLG. The ratio of FLG and MWCNT in the paper was varied from FLG-dominated to MWCNT-dominated in order to study the efficiency in improving electrical conductivity. A synergistic effect on electrical conductivity between 2D FLG and 1D MWCNT was demonstrated in the hybrid paper.

In an environmentally friendly approach, free-standing hybrid papers were fabricated by vacuum-assisted filtration of GO nanosheets and CNTs both suspended in water. The hybrid paper was further annealed at 800 $^{\circ}\text{C}$ to reduce GO sheets, thus obtaining graphene-CNT hybrid paper [34]. The CNTs are randomly dispersed between the graphene nanosheets (with graphene predominating), and hence high mechanical strength and flexibility are preserved for the papers. In such an assembly, the presence of CNTs is expected to play multiple roles including (1) preventing the restacking of graphene during the process of paper fabrication, thus allowing more effective contact between the electrolyte and the graphene in the interior of hybrid paper, (2) increasing cross-plane conductivity of the paper as CNTs also have high electrical conductivity and can closely contact with graphene. Specially, Fan et al. [35] reported a novel strategy to prepare densely packed graphene nanomesh–CNT hybrid film (GNCN) through a simple graphene etching process and subsequent vacuum-assisted filtration method. SEM observation (Fig. 2.7c) of the GNCN film reveals a layered and wrinkled structure through the entire cross section. High-resolution SEM image of the cross-sectional edge of GNCN film (Fig. 2.7d) shows that CNTs can serve as an effective “spacers” to prevent the restacking of the sheets that are closely stacked in a nearly parallel fashion, and also efficiently improve the overall electrical and mechanical properties of the film. TEM observation clearly exhibits nanomesh with the pore size of 1–2 nm (Fig. 2.7f) in the graphene sheet due to MnO_2 etching based on the reaction between permanganate (MnO_4^-) and carbon. The ion diffusion rate within this GNCN film is greatly enhanced due to the contribution of cross-plane diffusion

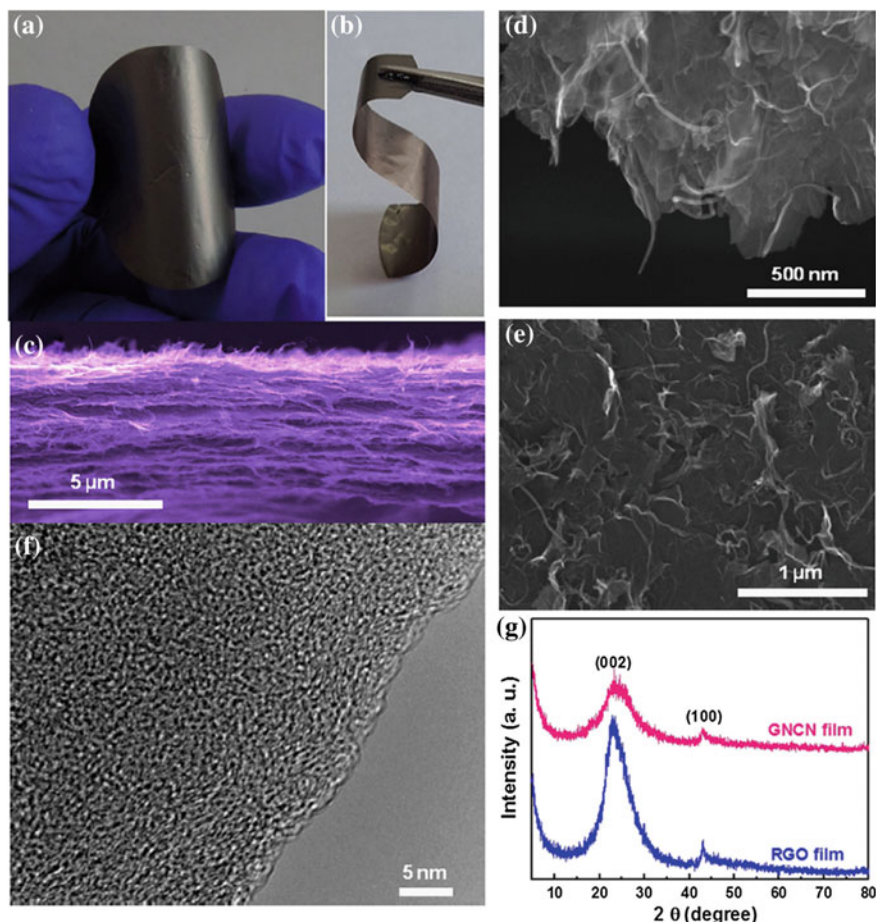


Fig. 2.7 **a** and **b** The optical images of the GNCN film. **c** The cross-section SEM image of the GNCN film. **d** High-resolution SEM image of the cross-sectional edge of GNCN film. **e** SEM image of the surface of the GNCN film. **f** TEM image of the GNCN film. **g** XRD patterns of the rGO and GNCN films. Reprinted with the permission from Ref. [35]. Copyright 2015 Elsevier

from graphene nanomesh and in-plane diffusion from graphene-CNT sandwiched structure. In addition, CNTs can also efficiently improve the overall electrical and mechanical properties of the hybrid film.

Instead of the compact layered structure, a thin graphene-CNT hybrid paper with 3D porous nanostructures was constructed by Liu and coworkers [36]. This porous nitrogen-doped graphene-CNT (p-N-GC) papers were prepared by removing polystyrene (PS) particle template, reducing GO sheets into graphene and achieving N-doping in one-step calcination. As shown in Fig. 2.8a, this paper with high flexibility is able to bend and held repeatedly. Sandwiched structures with CNTs incorporated between graphene sheets are obtained (Fig. 2.8b). The porous

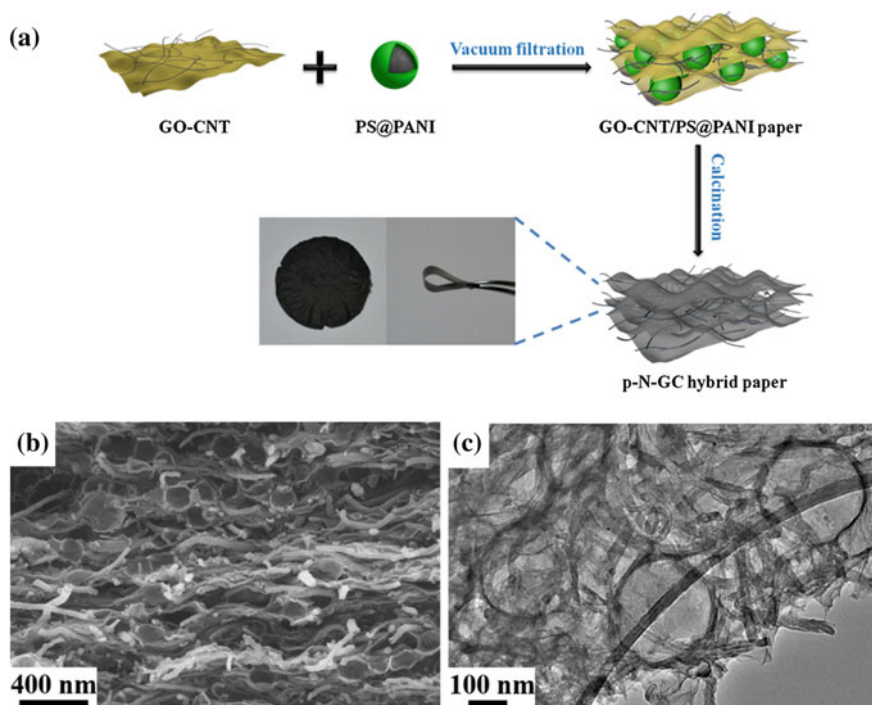


Fig. 2.8 **a** A schematic for the fabrication of porous N-doped graphene-CNT (p-N-GC) hybrid paper. Digital photos of the flexible p-N-GC paper with good flexibility. **b** SEM and **c** TEM images of p-N-GC hybrid paper. [Original citation]-Reprinted with the permission from Ref. [36]. Copyright 2015 Royal Society of Chemistry

nanostructures derived from removal of PS particles and graphene-CNT networks can be clearly seen from TEM observation (Fig. 2.8c). Here, CNTs can act as both the spacers and conductive linkers between individual graphene sheets, which can destroy the well-ordered structure of layered graphene, thus contributing to higher porosity and conductivity.

Although the assembly-based methods have succeeded in the fabrication of 2D or 3D hybrid nanostructures from graphene and CNTs due to their similar crystal structures and work functions, it in fact is still very difficult to assemble graphene layers and CNTs in the form of a hybrid film with controllable architecture at the nanometer scale. Within the last few years, efforts have been made to fabricate graphene-CNT hybrid films via spin coating or self-assembly of homogeneously mixed solutions of reduced GO and CNTs using surface functionalization techniques. Such hybrid films thus prepared consist of overlapped thick graphene aggregates with poor controllability of the nanoarchitecture, resulting in the

reduction of the transmittance of graphene film and the total surface area of the hybrids. Therefore, assembly of vertically aligned CNT pillars on a large-area graphene film is considered to be extremely important for constructing a new nanoarchitecture for future energy storage and electronic applications.

2.2 In Situ Method

The product of assembly processes is usually of lower quality that would ultimately affect the conductivity and surface area, though this method is simpler than in situ fabrication. Contrarily, in situ growth of graphene-CNT hybrids is more complicated, but holds better control of the quality of product, including their morphology, density, and orientation of the hybrid structures.

2.2.1 Chemical Vapor Deposition

This method can prepare hybrids with graphene and/or CNTs during a direct CVD growth, which can control the nanostructures by adjusting growth conditions [37–42]. In comparison to assembled hybrids, simple process without complicating steps and uniformly dispersed CNTs on graphene sheets can be achieved through in situ methods.

Through plasma-enhanced chemical vapor deposition (PECVD), graphene-CNT hybrid was prepared by employing CNTs as the substrate where defects in the CNTs formed nucleation sites and methane was cracked into free carbon, leading to few-layer graphene (FLG) sheets [43]. The host CNT and the as-grown FLG are inherently “fused” or chemically bonded together by sp^2 carbons, forming a single, total-carbon nanostructure with minimized graphene-CNT junctions. SEM image shows that FLGs were grown on the entire external surface of every single CNT (Fig. 2.9). Although the CNT stem was uniform in diameter, a much larger FLG corolla capped the tube tip (Fig. 2.9c), indicating that the FLGs grew faster on the tip portion of a vertical CNT than on its lower portion. HRTEM image shows an FLG sheet growing directly off a host CNT, and individual graphene layers of the FLG can be discerned. Besides, the lattice fringes of the FLG match with those of the host CNT, suggesting that the graphitic lattice formation of FLG initiated from the lattice of the CNT. The interlayer spacing for the CNT and the FLG in Fig. 2.9e are measured as 0.346 and 0.348 nm, respectively, which are consistent with the interlayer distance of ~ 0.34 nm for MWCNTs. This work with fusing FLG with CNT into a single unified structure shows a great step toward controlling the interfaces between constituent components in hybrid nanostructures.

The electronic and thermal conductivities of CNTs are greatly reduced in forest-like or entangled structures owing to the discontinuous contact between CNTs. To overcome this problem, Kim and coworkers developed a facile approach

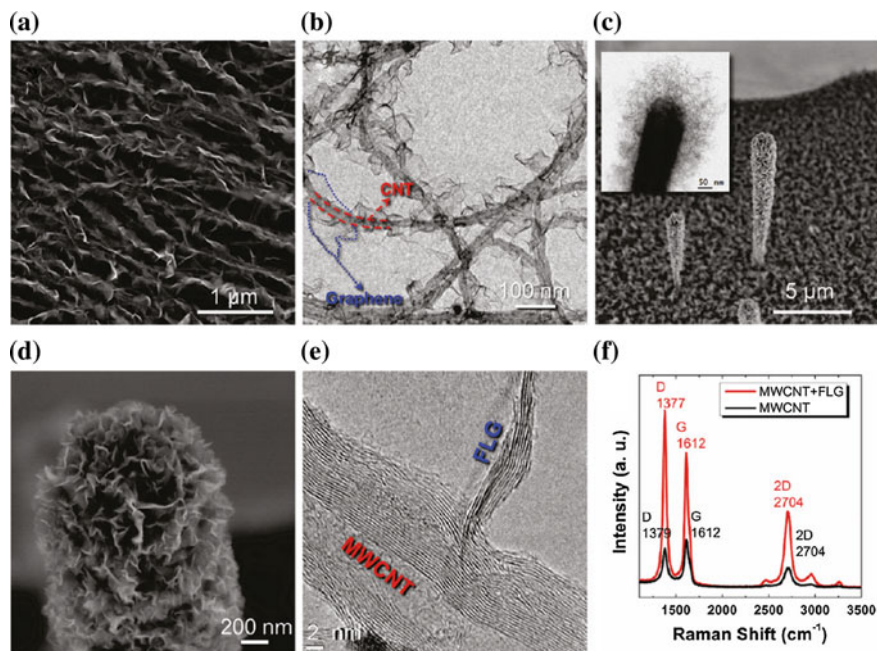


Fig. 2.9 **a** SEM image of CNT–FLG hybrid structures. **b** TEM image of FLGs grown on CNTs suspended on a Cu TEM grid. **c** SEM image of FLGs grown on vertically aligned CNTs; the inset is a TEM image of the tip of a CNT–FLG, where the CNT stem (*dark*) is clearly distinguished from FLGs (*bright*). **d** A close view of the CNT–FLG tip in panel **c**. **e** HRTEM image of a CNT–FLG structure showing that the FLG is inherently bonded to the host CNT. **f** Raman spectra of pristine CNT (*black*) and CNT–FLG (*red*) films. Reproduced with permission from Ref. [43]. Copyright 2011 American Chemical Society

to fabricate hierarchical hybrids of vertical and inverted CNT structures on graphene sheets [44]. A modification of this interesting approach was afterwards exploited for the formation of 3D nanostructures upon the vertical growth of CNTs pillars in between the graphene layers that become available with cobalt-decorated GO [45]. CNTs were incorporated uniformly between the graphene sheets but sparsely on the surface of GO sheets. In addition, the enlarged view of the hybrid material reveals that the distance between CNTs is about 100–200 nm, and the majority of the CNTs is less than 100 nm in length. Similarly, Zhao et al. [46] developed the fabrication of CNT-pillared GO and graphene structures with different length of CNTs (Fig. 2.10). The cross-sectional images of the samples show layer nanostructures of CNTs as nanopillars between the GO and graphene sheets. More CNTs can be obtained by enhancing the number of Ni catalysts, while shorter CNTs can be achieved by reducing the time of CVD growth. The CNT-pillared rGO composite materials exhibited an excellent visible light photocatalytic performance in degrading dye Rhodamine B because of the unique porous structure and the exceptional electron transfer property of graphene.

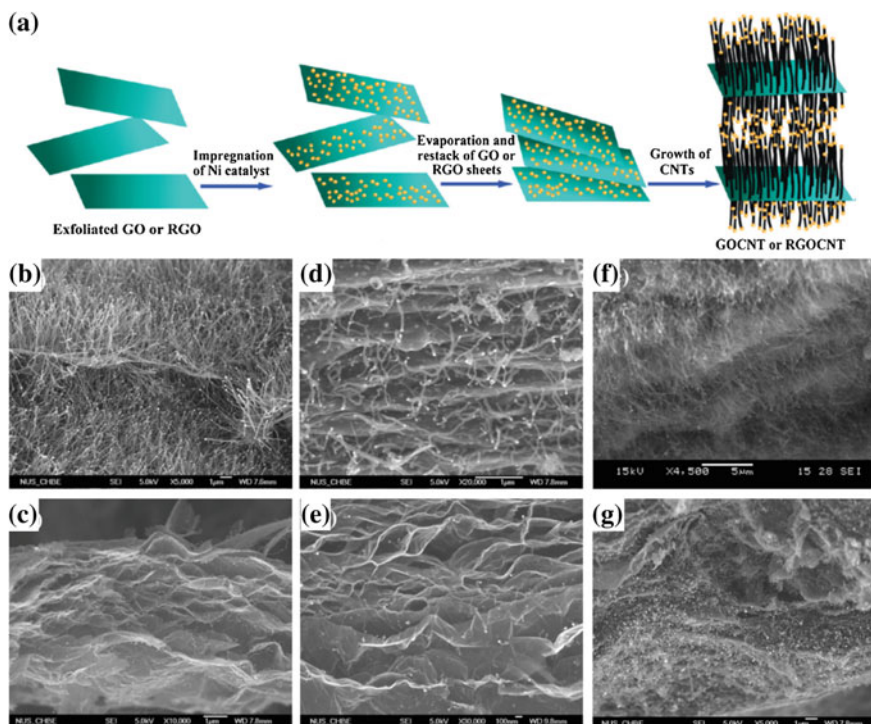


Fig. 2.10 a Experimental steps of pillaring GO and graphene platelets with MWCNTs. FESEM images of b GOCNT-30-17, c GOCNT-15-17, d GOCNT-30-9, e GOCNT-15-9, f RGOCNT-15-4, and g RGOCNT-15-0.6. The final samples are denoted as GOCNT-*X*-*Y* or RGOCNT-*X*-*Y* for the CNT-pillared GO and RGO composites, respectively. Here, *X* represents CVD time (15 or 30 min) while *Y* refers to the Ni catalyst loading expressed using the mass ratio of Ni/C. Reproduced with permission from Ref. [46]. Copyright 2010 American Chemical Society

In addition to directly growing CNTs on sheet-like graphene, an interesting work reported a CNT/crumpled graphene ball hybrid by direct growth of CNTs on the surface of crumpled graphene ball [47]. Unlike the previous report about graphene-CNT hybrids, the present hybrid has a unique hierarchical structure because the surface of crumpled graphene ball is decorated with porous CNT networks and thus has a variety of advantages for supercapacitor applications. In the first step, crumpled graphene ball/ Fe_3O_4 nanocrystal hybrids were produced by a one-pot ultrasonic nebulizer-based spray method. Specifically, the GO suspension with precursor ions (i.e., Fe^{3+}) was nebulized to generate aerosol droplets that flowed through a tube furnace. Because the average size of the generated droplets was on the order of micrometers, the solvents rapidly evaporated in the tube furnace, leading to the shrinkage of GO sheets and the subsequent compression of GO sheets into crumpled balls with a submicrometer size. Simultaneously, Fe_3O_4 nanocrystals grew from the precursor Fe^{3+} ions and deposited on both external and

internal surfaces of crumpled graphene balls during the solvent evaporation and the GO crumpling process. In the second step, CNTs were grown on the surface of crumpled graphene ball through a CVD method with Fe as the catalyst. The typical growth process included a reduction of the crumpled graphene ball/ Fe_3O_4 hybrids with H_2 and a CVD growth of CNTs with C_2H_2 gas as the carbon source.

CNTs can also be grown on 3D graphene macroscopic structures [48, 49]. The 3D graphene-CNT hybrids were prepared by a two-step CVD approach. Using nickel (Ni) foam as the substrate and ethanol as the precursor, graphene foam was first fabricated, which was then dipped into NiCl_2 solution to obtain the Ni substrates for the CVD growth of graphene-CNT hybrids (Fig. 2.11a). Figure 2.11b, c shows the SEM images of graphene foam that exhibits macroporous structures. Using graphene foam as the 3D catalyst support for CVD growth of CNTs, CNT mesh grows evenly on the graphene foam (Fig. 2.11d, e). The thickness of CNT layer is 5.0 μm , and the inner and outer diameters of as-prepared CNTs are ~ 50 and ~ 85 nm, respectively. This template-directed CVD method is versatile and scalable, and can be an effective strategy for fabricating a broad class of 3D macroscopic graphene-CNT hybrids that possess excellent properties and great potential for novel applications.

Instead of growing CNTs above graphene sheets, CNTs can also grow from the bottom of the graphene surface [50]. Thin film (about 20 nm) of Fe catalysts was deposited on a SiO_2/Si substrate, and the CVD growth was performed at 700 $^\circ\text{C}$ by employing C_2H_4 and Ar as gas precursors. The corresponding SEM image (Fig. 2.12a) shows that vertically aligned MWCNTs were grown on the SiO_2/Si substrate with graphene film on top of it. The thickness of the graphene film varies from 15 to 20 nm, and the average length and diameter of MWCNTs was about 30–40 μm and 10 nm, respectively. The deposit, nucleation, and growth of catalysts, as well as diffusion of carbon atoms, all have a great influence on the CVD growth of MWCNT. The size of catalysts is related to the morphology and structure of resulting carbon hybrids. With varying thickness of catalyst film (10, 20, and 30 nm), it is found that the growth of graphene-CNT hybrid film only happened from 20 nm catalyst film while no trace of hybrid film was seen below 10 nm or above 30 nm catalyst areas. Instead, in the 10 nm and 30 nm thin film area, thin MWCNT and thick aggregated particles were seen, respectively.

A similar structure was reported by Zhang and coworkers through a two-step CVD growth [51]. First, few-layer graphene was grown on a Cu foil at 1000 $^\circ\text{C}$ with Ar, H_2 , and CH_4 as gas precursors. After graphene was transferred onto PMMA film and the Cu foil was etched away, the resulting graphene/PMMA film was then transferred onto a $\text{Fe}/\text{Al}_2\text{O}_3/\text{SiO}_2/\text{Si}$ substrate. After the removal of PMMA, the graphene film on substrate was then used to conduct the CVD growth of CNT arrays with Ar, H_2 , and C_2H_4 at 750 $^\circ\text{C}$. The graphene broke into small flakes and covered the tips of as-grown vertically aligned CNT arrays, forming “jellyfish” nanostructures. Besides, the growth of CNTs would be affected by the existence of graphene. The growth of CNTs in the graphene region occurred later but faster than that out of the graphene region, which resulted from the enhanced diffusion of gas precursors due to the breakage of graphene film.

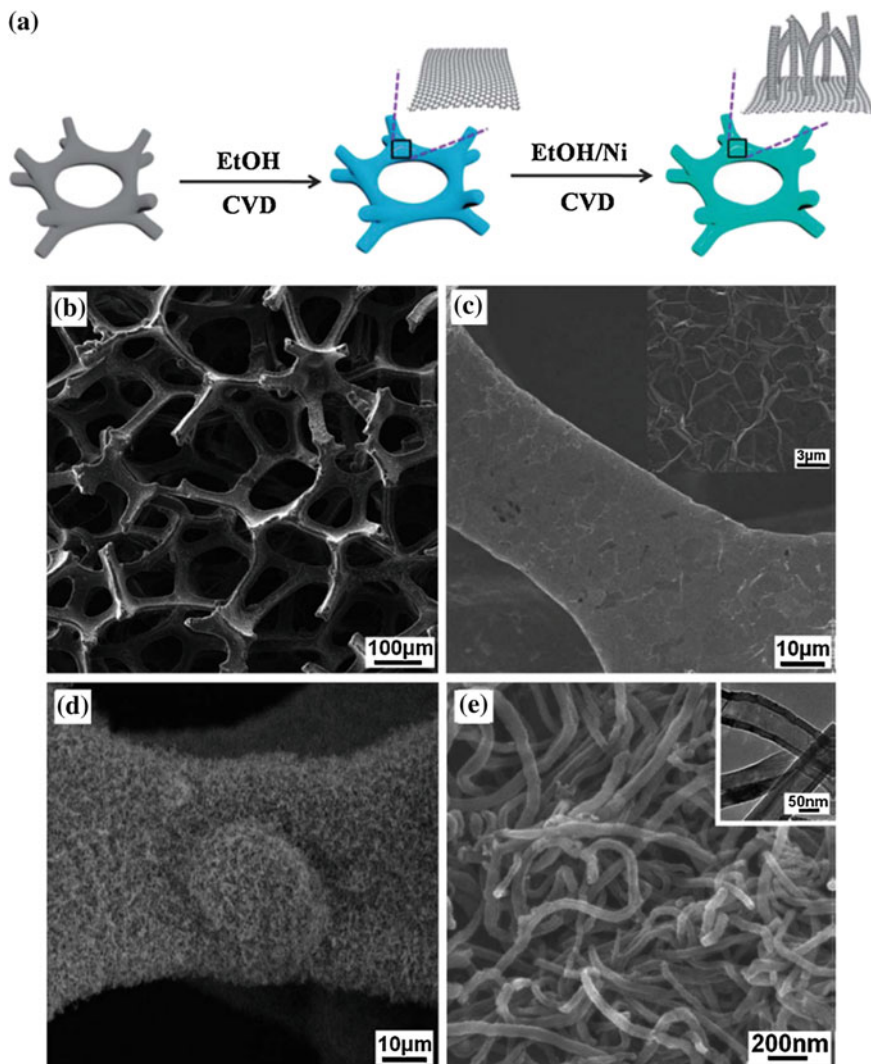


Fig. 2.11 **a** A schematic illustration of the fabricated 3D CNT–graphene–Ni hybrids. Reproduced with permission from Ref. [49]. Copyright 2014 Royal Society of Chemistry. **b** SEM images of bare 3D graphene. **c** SEM image on the surface of graphene skeleton. The inset is a higher magnification display. **d** SEM image of the skeleton of the 3D graphene-CNT hybrid. **e** SEM image of CNT mesh grown on graphene foam. The inset depicts the TEM image of individual CNTs. Reproduced with permission from Ref. [48]. Copyright 2012 Royal Society of Chemistry

The CVD growth of CNT arrays onto both sides of graphene film was reported, with vertically aligned CNT arrays grown beneath graphene (B-CNT) and on the top surface of the graphene (T-CNT) with an additional layer of catalyst [52]. The whole preparation process of the sandwiched T-CNT/graphene/B-CNT nanostructures is

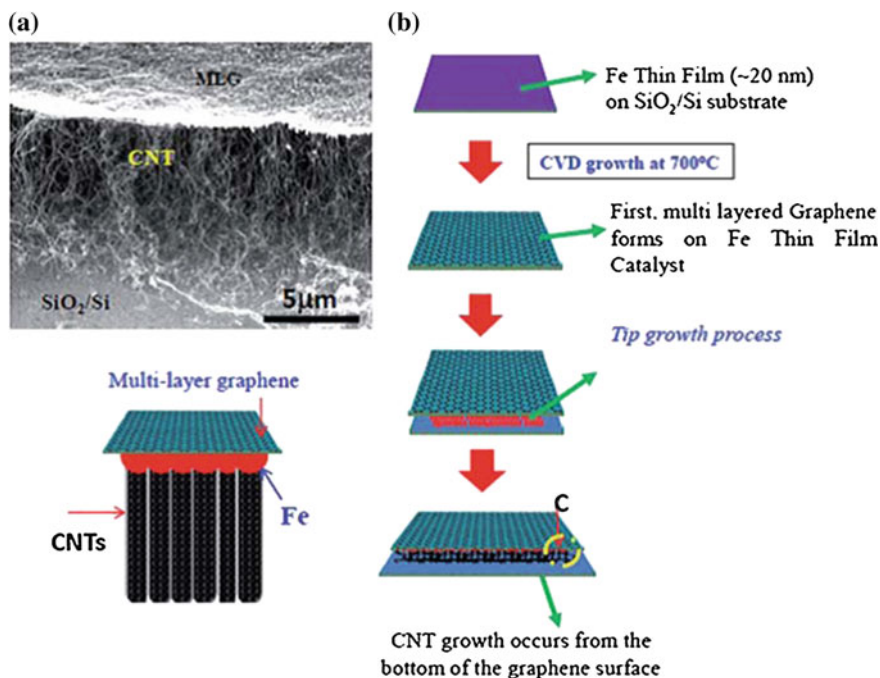


Fig. 2.12 **a** SEM image of as-prepared multilayered graphene film–CNT hybrids on the SiO_2/Si substrate. **b** Schematic illustration of the preparation of graphene–CNT films. Reproduced with permission from Ref. [50]. Copyright 2011 Royal Society of Chemistry

illustrated in Fig. 2.13a. The side-view SEM images of the sandwiched structure at different magnifications (Fig. 2.13b, c) show that the B-CNT with a height of about $15\ \mu\text{m}$ is mostly straight, just like those CNTs grown without graphene film on top. The as-grown T-CNT is obviously curved, and the distinct interface between T-CNT and B-CNT belongs to the layered graphene marked by the dashed rectangle in Fig. 2.13d. During the CVD growth, the deposit of catalyst are very important with Fe catalysts deposited on graphene and the Al_2O_3 buffer layer on top of Fe, which ensures the subsequent tip growth of B-CNT lifting the $\text{Al}_2\text{O}_3/\text{Fe}$ film. Besides, in order to acquire CNTs contacted with both sides of graphene, the tip-growth CNT carpets on top of graphene and base-growth CNT carpets underneath graphene are needed ($\text{Al}_2\text{O}_3/\text{Fe}/\text{T-CNT}/\text{graphene}/\text{B-CNT}/\text{Fe}/\text{Al}_2\text{O}_3$). The designed catalyst/buffer $\text{Al}_2\text{O}_3/\text{Fe}/\text{graphene}/\text{Fe}/\text{Al}_2\text{O}_3$ film can ensure simultaneous growth of T-CNT and B-CNT in the CVD process.

As discussed above, graphene-CNT hybrids can be formed by directly growing graphene on CNTs and vertically aligned CNTs above or beneath graphene or on both sides of graphene. Apart from this, graphene-CNT hybrids can be synthesized simultaneously in a single CVD step using a mixed catalyst due to the similar growth process for both components. CNTs were generally prone to grow on nanostructured

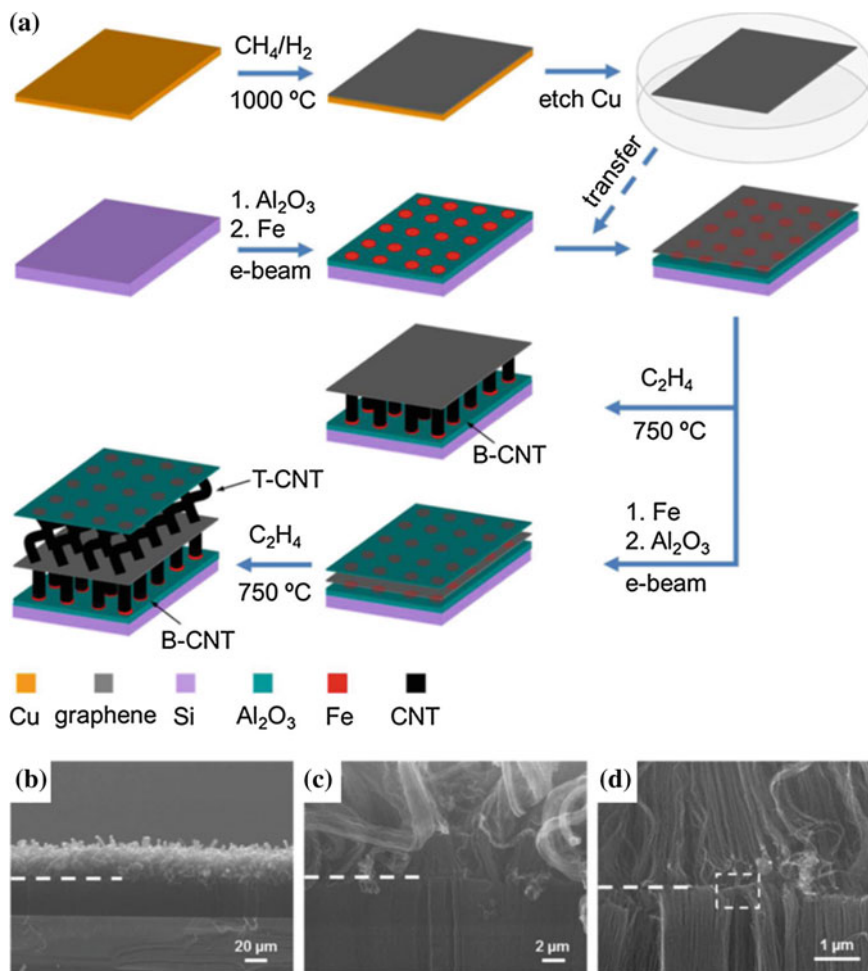


Fig. 2.13 **a** A schematic for the preparation of graphene/B-CNT and T-CNT/graphene/B-CNT hybrids. **b** CNTs grown underneath graphene to lift up the graphene film, or CNTs grown both **c** underneath and **d** on top of the graphene film. Reproduced with permission from Ref. [52]. Copyright 2016 American Chemical Society

metal catalyst particles while graphene preferred to grow on the Cu or metal oxide film. In this one-step approach to grow both of graphene and CNTs, the catalysts (e.g., Fe and Ni) are deposited on the growth substrate of graphene (e.g., copper foil and MgO) by thin film evaporation methods or immersing in metal salt solution. For instance, Ozkan et al. [53] described the fabrication of pillared graphene nanostructures (PGNs) comprised of stacked CNT pillars on large-area graphene layers in one step. CVD growth process was carried out using C_2H_2 or CH_4 gas as a carbon source to fabricate a large-area PGN with controlled architecture on a

Fe-nanoparticle-decorated thin layer (≈ 500 nm) of e-beam-evaporated copper film deposited on a SiO_2/Si substrate. The highly crystalline interface between the CNT pillar and graphene floor confirmed the seamless contact between the two carbon allotropes. Copper is able to function as catalyst for the CVD growth of graphene and CNT. Chen et al. [54] reported a simple approach to synthesize highly conductive graphene-CNT hybrid materials by one-step CVD growth on Si nanoparticle coated copper foil. It is conceivable that, at high temperature (800°C), Cu may evaporate, precipitate, and aggregate on Si NPs to serve as the nanocatalysts for growth of CNTs. The bamboo-like CNTs can be acquired with homogeneous coverage on graphene. In another report, lamella-like mixed catalyst (Fe/MgO and MgO) obtained from hydrothermal route can be used for the CVD growth of graphene-CNT hybrids (Fig. 2.14a) [55]. MgO layers acted as templates for the growth of graphene, and Fe particles on the MgO layers catalyzed the growth of single- or double-walled CNTs. The composition of graphene with the CNT network was clearly observed by TEM images (Fig. 2.14b, c). The distribution of graphene and CNTs in the graphene-CNT hybrid was quite even in a wide-view field. And the graphene-CNT hybrid possesses a porous morphology, in which the network of CNTs can be seen. The blurred textures of the CNTs indicate that the CNTs are covered by graphene.

Nevertheless, the mixed catalysts rather resemble in situ mixing of the as-prepared graphene and CNTs than the in situ growth of graphene/CNT hybrids. Instead of mixed catalysts, bifunctional catalyst was used to prepare graphene-CNT

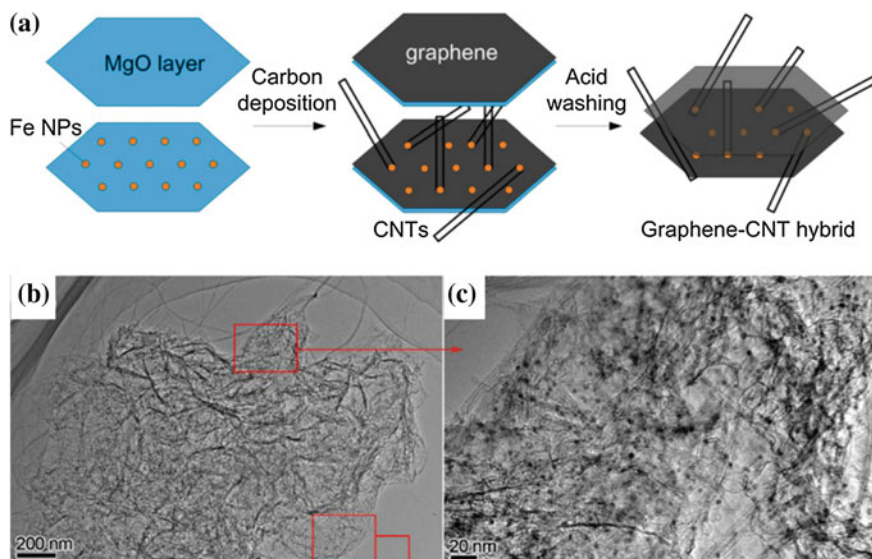


Fig. 2.14 a A schematic illustration of one-step CVD synthesis of the graphene-CNT hybrid material; b, c TEM images of graphene-CNT hybrid. Reprinted with the permission from Ref. [55]. Copyright 2012 Elsevier

hybrid, which could serve as catalysts for both CNTs and graphene growth [56–61]. Typically, a layered material embedded with metal nanoparticles in their interlayer spaces serves as the bifunctional catalysts for the growth of aligned CNT/graphene sandwiches. FeMo/vermiculite composed of exfoliated vermiculite with FeMo nanoparticles supported on their interlayer surfaces was used as the bifunctional catalysts for the in situ growth of aligned CNT/graphene sandwiches (Fig. 2.15a) [56]. The bifunctional FeMo/vermiculite catalyst is very effective to obtain high-quality aligned CNTs and graphene with a direct and intimate connection. The vermiculite is a kind of layered natural aluminosilicate that inherently contains various metal elements (e.g., Fe, Mg, Al). After reduction under H_2 atmosphere, Fe nanoparticles were formed on the pristine vermiculite sheets and promoted the CNT growth. CVD of ethylene at a low temperature of 650 °C was first carried out to achieve the intercalated growth of aligned CNTs on the metal catalysts. The growth of aligned CNTs also is beneficial to the metal nanoparticles with stable size. The vermiculite layers were pushed away from each other but their morphologies were well preserved, which provided diffusion pathway for the carbon source to reach the vermiculite layer for uniform deposition of graphene layers on each vermiculite layers at a high temperature of 950 °C. Sandwiched aligned CNT/graphene hybrids composed of alternating aligned CNTs and graphene materials were available by removal of the catalyst. With the intercalation of aligned CNTs and graphene into vermiculite, the flat sheets of vermiculites were obviously expanded in length (Fig. 2.15b). SEM images shown in Fig. 2.15c, d reveal a periodical sandwich-like structure that aligned CNTs with a uniform length and good alignment perpendicularly grown among the interlayer spaces of vermiculite sheets. Aligned CNT/graphene sandwiches with high carbon purity of 98.3 wt% are available after the removal of the FeMo/vermiculite catalysts by facile acid treatments (Fig. 2.15e). The as-obtained aligned CNT/graphene sandwiches exhibit the morphology of alternating aligned CNTs and continuous graphene sheets (Fig. 2.15f). There are nanogaps between the two opposite aligned CNT/graphene structural units, which are resulted by the removal of the vermiculite flakes (Fig. 2.15g). The aligned CNTs were perpendicularly connected to the graphene sheet at the bottom, and two opposite structural units joined in the middle through interlink of CNTs due to the opposite growth of two aligned CNT bundles. The aligned CNTs were multiwalled with a uniform length of 7–13 μm after 15 min CVD growth at 650 °C. The layer of graphene sheets was ca. 2–5 after 30 min deposition at 950 °C. The as-obtained aligned CNT/graphene sandwiches are of abundant porosity, excellent structural stability, and a hierarchical resilient structure, which render them as promising materials for mechanical energy storage. This bottom-up strategy that integrates CNTs and graphene into 3D networks enhances their intrinsic excellent properties and performance, and can even bridge the microscopic structure to meso- and macroscale applications.

The same group also reported another bifunctional catalyst, layered double hydroxides (LDHs) nanosheets as layered substrates for the CVD growth of

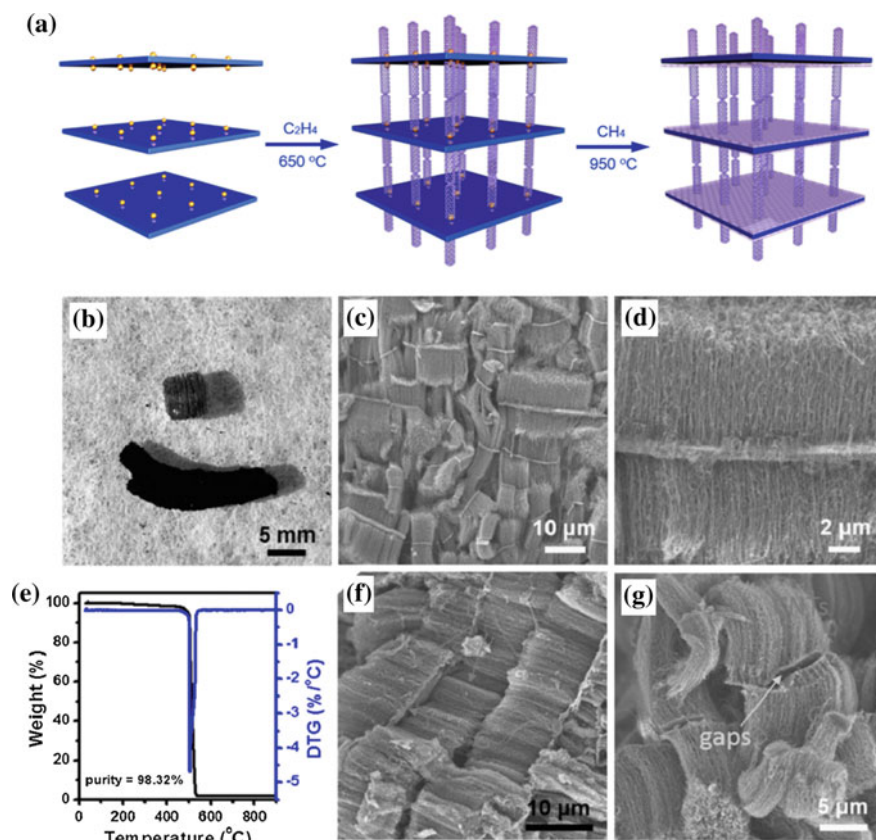


Fig. 2.15 **a** A schematic illustration for the synthesis of aligned CNT/graphene sandwiches on bifunctional catalysts. **b** Digital photograph of a block of vermiculite catalyst (*brown*) and aligned CNT/graphene sandwich. **c**, **d** SEM images of aligned CNT/graphene/vermiculite composite. **e** TGA curve of the aligned CNT/graphene sandwiches under O_2 atmosphere. **f**, **g** SEM images of the aligned CNT/graphene sandwiches. The arrowed gaps were generated after the removal of the vermiculite flake. Reprinted with the permission from Ref. [60]. Copyright 2014 Elsevier

graphene-CNT hybrids at high temperature [58]. Hydrotalcite-like LDHs materials, comprised of positively charged layers and charge-balancing interlayer anions, are considered as excellent catalysts for the CVD growth of graphene/SWCNT (G/SWCNT) hybrids. The flake nanostructures of LDHs can provide hard template for the growth of graphene, while their high density of metal nanoparticles and good thermal stability allow CVD growth of SWCNT simultaneously. The preparation of G/SWCNT hybrids is shown in Fig. 2.16a. The CVD growth of graphene on FeMgAl LDH flakes were conducted at 950 °C for 10 min, when the as-generated hydrogen derived from the decomposed hydrocarbons could reduce

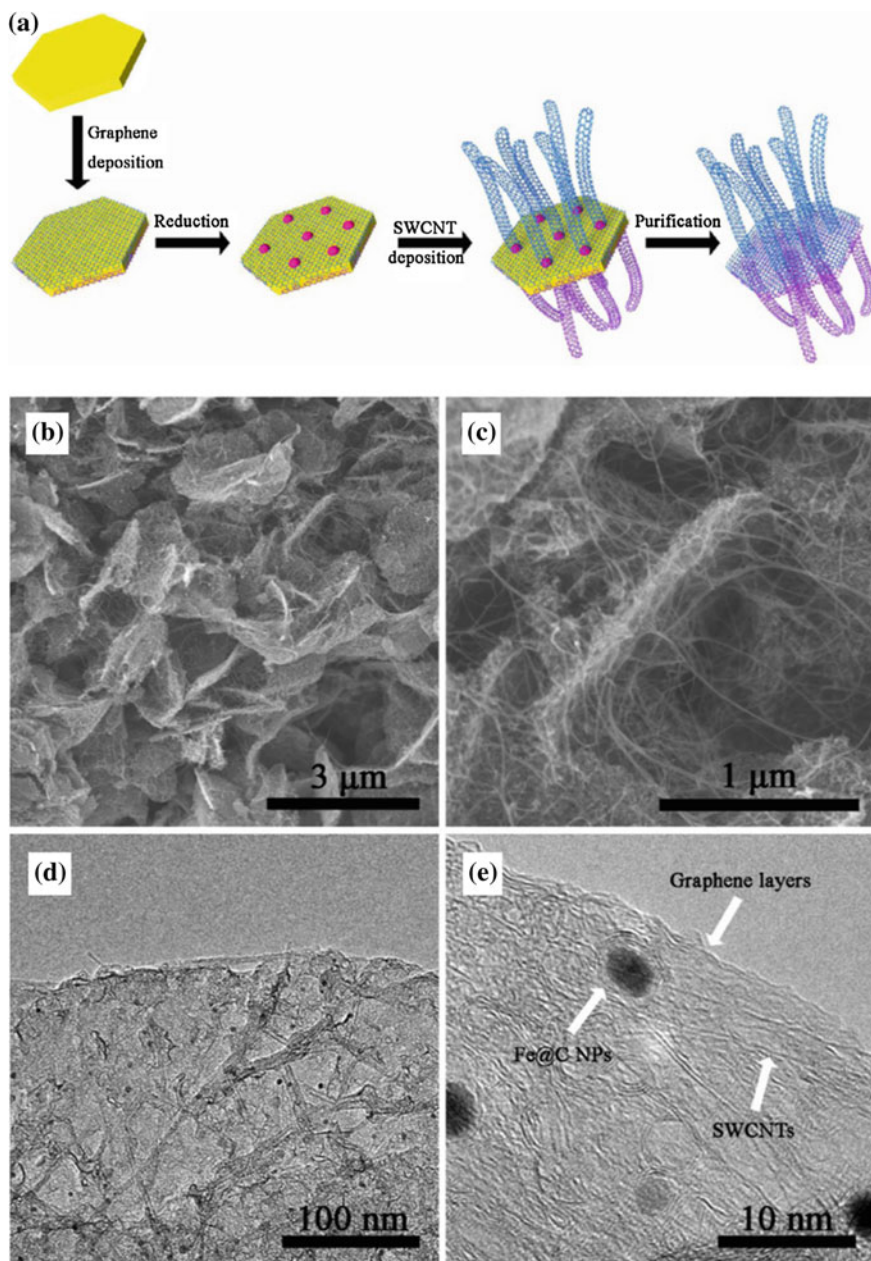


Fig. 2.16 **a** A schematic of the CVD growth of G/SWCNT hybrids on LDH flakes. **b**, **c** SEM images of the G/SWCNT hybrids; **d** TEM and **e** HRTEM images of the G/SWCNT hybrids. Reproduced with permission from Ref. [58]. Copyright 2009 American Chemical Society (ACS AuthorChoice)

the LDHs to form Fe catalysts that enabled the continuous growth of SWCNTs. After removing the calcined LDH flakes, interlinked G/SWCNT hybrids with most of SWCNTs grown onto both sides of graphene can be obtained (Fig. 2.16b, c). From the TEM images in Fig. 2.16d, e, few-layer graphene sheets (less than four layers), SWCNTs, and some left Fe particles are seen. Further study about the CVD growth mechanism of G/SWCNT hybrids on layered double oxide (LDO) catalysts was carried out to analyze the growth of CNTs, graphene, and amorphous carbon. During the CVD growth process, graphene was first deposited on LDO flakes due to the addition of CH_4 , while as-generated H_2 derived from decomposed CH_4 enable reducing the LDO flakes for the formation of Fe nanoparticles that induce the growth of SWCNTs. As the carbon atoms are highly soluble at 950°C , they were dissolved in Fe particles and this has led to the growth of SWCNTs within the Fe particles, which achieved tight interconnection between SWCNTs and graphene.

2.2.2 Unzipping

As discussed in Chap. 1, it is a facile and scalable pathway to use chemical unzipping for fabrication of graphene nanoribbons (GNRs). Tour's group [62] developed an oxidation approach to unzip CNTs along with their axis, and the yield of GNRs is high and efficient (approaching 100 %). The resulting GNRs have high solubility in polar solvents owing to their oxidized edges that can be chemically reduced to regain their conductivity. The usage of oxidant have a big influence on the degree of unzipping, thus making it easy to prepare CNTs/GNRs hybrids with different ratio of CNTs to GNRs [63].

Liu et al. [64–67] reported a facile unzipping method to fabricate graphene oxide nanoribbon/carbon nanotube (GONR/CNT) hybrids (Fig. 2.17a). With the MWCNTs partially unzipped, the left MWCNTs can connect with as-prepared GNRs to form 3D interconnected carbon networks. After being chemically reduced by hydrazine hydrate, GNR/CNT hybrids can be acquired with enhanced conductivity of 120 S cm^{-1} compared with that of CNTs (65 S cm^{-1}) [64]. As shown in Fig. 2.17c, different weight percentage of GONRs in GONR/CNT hybrids can be readily prepared and determined by XRD patterns, where the GONR peak ($2\theta = 11.28^\circ$) increased while the CNT peak ($2\theta = 26.18^\circ$) decreased. A relationship curve can be obtained from the intensity of their characteristic peaks, which can give the GONR weight ratios of as-prepared GONR/CNT hybrids as 16, 55, and 85 %, respectively. For simplicity, they were defined as $\text{GONR}_{16\%}/\text{CNT}$, $\text{GONR}_{55\%}/\text{CNT}$, and $\text{GONR}_{85\%}/\text{CNT}$.

The TEM and SEM images (Fig. 2.18) of GNR/CNT hybrids with different GNR weight ratios show that GNRs are connected with CNTs in the hybrids and more GNRs are obviously seen when the unzipping degree increased. Employing

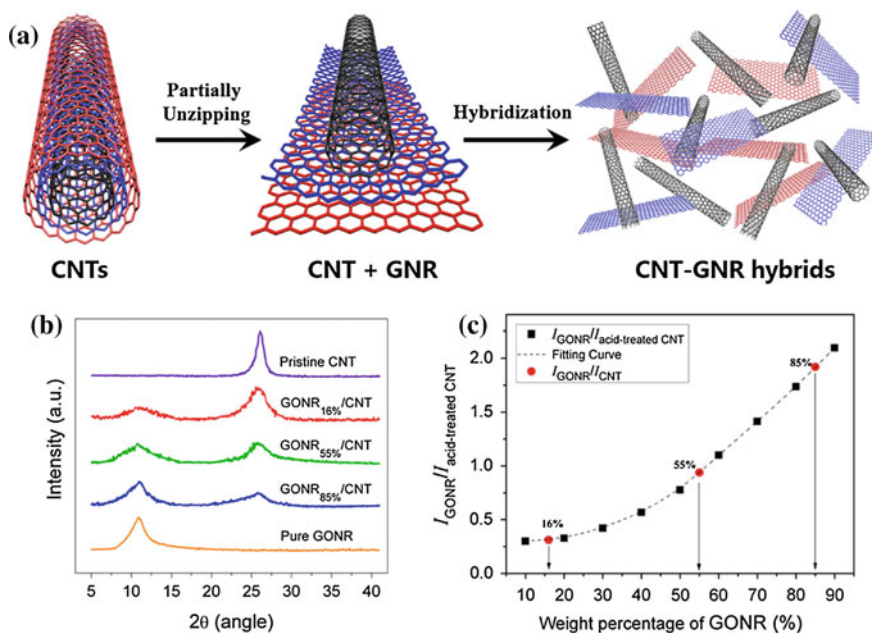


Fig. 2.17 **a** Schematic of the fabrication process of the GNR/CNT hybrid. **b** XRD patterns of pristine CNTs, GONR/CNT hybrids with different GONR weight ratios and pure GONR. **c** Calculation of GONR weight ratio in GONR/CNT hybrids based on the relationship between GONR weight percentage and intensity ratio of characteristic peaks in their XRD patterns. Reproduced with permission from Ref. [64]. Copyright 2010 John Wiley & Sons, Inc

this GNR/CNT hybrids as fillers to enhance the mechanical properties of polymer composites was reported [68]. Benefiting from the excellent stability of GNR/CNT hybrids in *N,N*-dimethylformamide solution, uniform dispersion of GNR/CNT hybrids in polyurethane (TPU) can be readily obtained through the solution casting method. With 1.0 wt% GNR/CNT hybrids incorporated, the tensile strength and Young's modulus of GNR/CNT/TPU composites are increased by 184 % (88.0 MPa) and 81 % (59.7 MPa), respectively, compared with those of pure TPU polymer. These results are ascribed to the excellent dispersion of GNR/CNT hybrids within the TPU matrix, as well as the fine interfacial connection between the hybrids and polymer matrix. It is also revealed that the toughness of TPU/(1.0 wt% GNR/CNT) composites enhanced by 260 % to 247 J g⁻¹ compared with that of pure TPU (68 J g⁻¹). The synergistic effect derived from interconnected structures, along with the stretching and interface sliding between CNTs and GNRs, all contribute to the significantly improved toughness of TPU/(1.0 wt% GNR/CNT) composites.

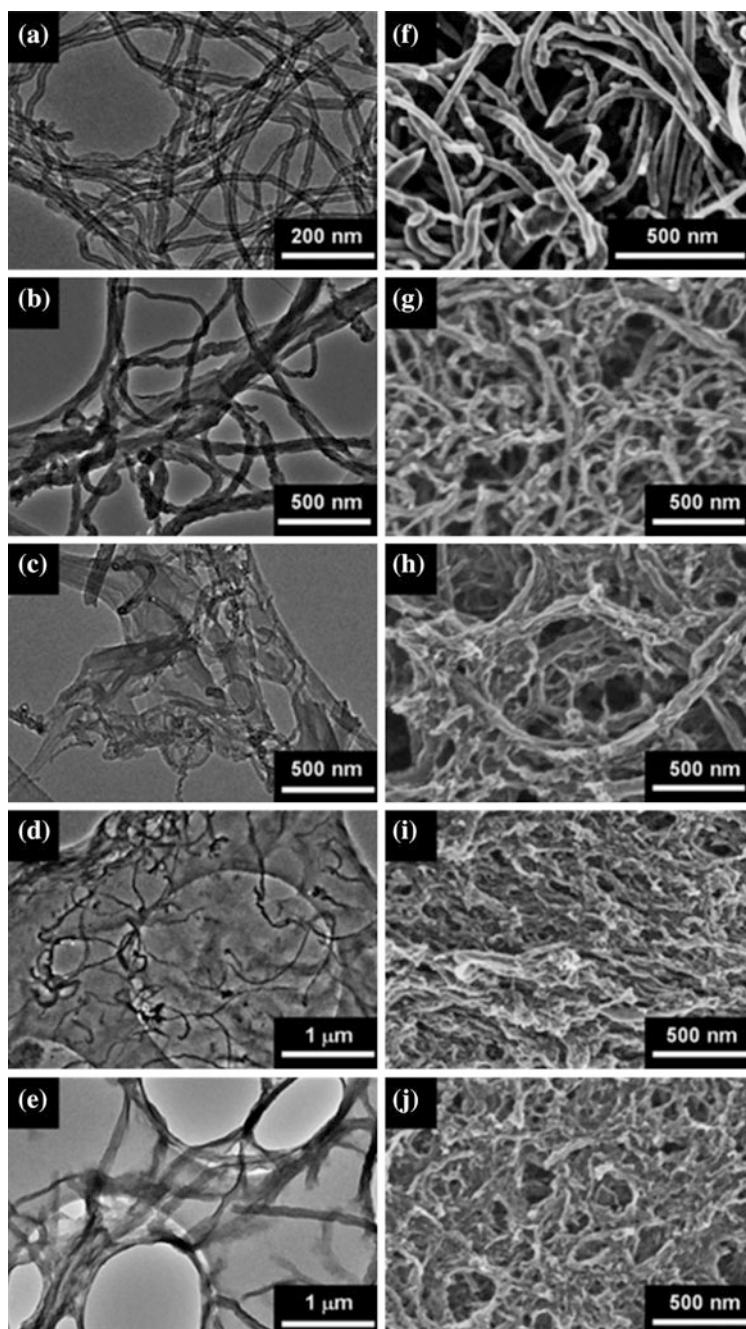


Fig. 2.18 a–e TEM images of CNTs, GNR/CNT hybrids with increasing GNR weight percentages (16, 55, 85 %), and pure GNR, respectively. f–j SEM images corresponding to a–e, respectively. Reproduced with permission from Ref. [64]. Copyright 2010 John Wiley & Sons, Inc

References

1. Badhulika S, Terse-Thakoor T, Villarreal C, Mulchandani A (2015) Graphene hybrids: synthesis strategies and applications in sensors and sensitized solar cells. *Front Chem* 3:38
2. Nardecchia S, Carriazo D, Luisa Ferrer M, Gutierrez MC, Del Monte F (2013) Three dimensional macroporous architectures and aerogels built of carbon nanotubes and/or graphene: synthesis and applications. *Chem Soc Rev* 42:794–830
3. Kong HX (2013) Hybrids of carbon nanotubes and graphene/graphene oxide. *Curr Opin Solid State Mater Sci* 17:31–37
4. Mani V, Chen SM, Lou BS (2013) Three dimensional graphene oxide-carbon nanotubes and graphene-carbon nanotubes hybrids. *Int J Electrochem Sci* 8:11641–11660
5. Lee WJ, Maiti UN, Lee JM, Lim J, Han TH, Kim SO (2014) Nitrogen-doped carbon nanotubes and graphene composite structures for energy and catalytic applications. *Chem Commun* 50:6818–6830
6. Zhang C, Liu TX (2012) A review on hybridization modification of graphene and its polymer nanocomposites. *Chin Sci Bull* 57:3010–3021
7. Qiu L, Yang X, Gou X, Yang W, Ma Z, Wallace GG, Li D (2010) Dispersing carbon nanotubes with graphene oxide in water and synergistic effects between graphene derivatives. *Chem Eur J* 16:10653–10658
8. Zhang C, Ren LL, Wang XY, Liu TX (2010) Graphene oxide-assisted dispersion of pristine multiwalled carbon nanotubes in aqueous media. *J Phys Chem C* 114:11435–11440
9. Tian L, Mezziani MJ, Lu F, Kong CY, Cao L, Thorne TJ, Sun Y (2010) Graphene oxides for homogeneous dispersion of carbon nanotubes. *ACS Appl Mater Interfaces* 2:3217–3222
10. Liu Y, Feng Q, Xie X, Ye X (2011) The production of flexible and transparent conductive films of carbon nanotube/graphene networks coordinated by divalent metal (Cu, Ca or Mg) ions. *Carbon* 49:3371–3375
11. Pan Y, Bao H, Li L (2011) Noncovalently functionalized multiwalled carbon nanotubes by chitosan-grafted reduced graphene oxide and their synergistic reinforcing effects in chitosan films. *ACS Appl Mater Interfaces* 3:4819–4830
12. Kotal M, Bhowmick AK (2013) Multifunctional hybrid materials based on carbon nanotube chemically bonded to reduced graphene oxide. *J Phys Chem C* 117:25865–25875
13. Dong X, Xing G, Chan-Park MB, Shi W, Xiao N, Wang J, Yan Q, Sum TC, Huang W, Chen P (2011) The formation of a carbon nanotube–graphene oxide core–shell structure and its possible applications. *Carbon* 49:5071–5078
14. Liu Y, Min D (2010) Preparation of scrolled graphene oxides with multi-walled carbon nanotube templates. *Carbon* 48:4283–4288
15. Tung VC, Chen L, Allen MJ, Wassei JK, Nelson K, Kaner RB, Yang Y (2009) Low-temperature solution processing of graphene–carbon nanotube hybrid materials for high-performance transparent conductors. *Nano Lett* 9:1949–1955
16. Zhang C, Huang S, Tjiu WW, Fan W, Liu TX (2012) Facile preparation of water-dispersible graphene sheets stabilized by acid-treated multi-walled carbon nanotubes and their poly(vinyl alcohol) composites. *J Mater Chem* 22:2427–2434
17. Li YQ, Yang TY, Yu T, Zheng LX, Liao K (2011) Synergistic effect of hybrid carbon nanotube-graphene oxide as a nanofiller in enhancing the mechanical properties of PVA composites. *J Mater Chem* 21:10844–10851
18. Shin MK, Lee B, Kim SH, Lee JA, Spinks GM, Gambhir S, Wallace GG, Kozlov ME, Baughman RH, Kim SJ (2012) Synergistic toughening of composite fibres by self-alignment of reduced graphene oxide and carbon nanotubes. *Nat Commun* 3:650
19. Wang RR, Sun J, Gao L, Xu CH, Zhang J (2011) Fibrous nanocomposites of carbon nanotubes and graphene-oxide with synergetic mechanical and actutive performance. *Chem Commun* 47:8650
20. Luo JY, Tung VC, Koltonow AR, Jang HD, Huang JX (2012) Graphene oxide based conductive glue as a binder for ultracapacitor electrodes. *J Mater Chem* 22:12993–12996

21. Ahmad I, Khan U, Gun'Ko YK (2011) Graphene, carbon nanotube and ionic liquid mixtures: towards new quasi-solid state electrolytes for dye sensitised solar cells. *J Mater Chem* 21:16990–16996
22. Shakir I (2014) High energy density based flexible electrochemical supercapacitors from layer-by-layer assembled multiwall carbon nanotubes and graphene. *Electrochim Acta* 129:396–400
23. Wang SC, Yang J, Zhou XY, Li J (2013) Layer-by-layer assembled sandwich-like carbon nanotubes/graphene oxide composite as high-performance electrodes for lithium-ion batteries. *Int J Electrochem Sci* 8:9692–9703
24. Liu Y, Liu Y, Feng HB, Wu YM, Joshi L, Zeng XQ, Li JH (2012) Layer-by-layer assembly of chemical reduced graphene and carbon nanotubes for sensitive electrochemical immunoassay. *Biosens Bioelectron* 35:63–68
25. Kim YK, Min DH (2009) Durable large-area thin films of graphene/carbon nanotube double layers as a transparent electrode. *Langmuir* 25:11302–11306
26. Hong T, Lee DW, Choi HJ, Shin HS, Kim B (2010) Transparent, flexible conducting hybrid multilayer thin films of multiwalled carbon nanotubes with graphene nanosheets. *ACS Nano* 4:3861–3868
27. Yu DS, Dai LM (2010) Self-assembled graphene/carbon nanotube hybrid films for supercapacitors. *J Phys Chem Lett* 1:467–470
28. Dikin DA, Stankovich S, Zimney EJ, Piner RD, Dommett G, Evmenenko G, Nguyen ST, Ruoff RS (2007) Preparation and characterization of graphene oxide paper. *Nature* 448:457–460
29. Zhang C, Tjiu WW, Liu TX (2013) All-carbon composite paper as a flexible conducting substrate for the direct growth of polyaniline particles and its applications in supercapacitors. *Polym Chem* 4:5785–5792
30. Huang J, Xu Z, Abouali S, Akbari Garakani M, Kim J (2016) Porous graphene oxide/carbon nanotube hybrid films as interlayer for lithium-sulfur batteries. *Carbon* 99:624–632
31. Chen X, Qiu M, Ding H, Fu K, Fan Y (2016) A reduced graphene oxide nanofiltration membrane intercalated by well-dispersed carbon nanotubes for drinking water purification. *Nanoscale* 8:5696–5705
32. Khan U, O'Connor I, Gun'Ko YK, Coleman JN (2010) The preparation of hybrid films of carbon nanotubes and nano-graphite/graphene with excellent mechanical and electrical properties. *Carbon* 48:2825–2830
33. Tang Y, Gou JH (2010) Synergistic effect on electrical conductivity of few-layer graphene/multi-walled carbon nanotube paper. *Mater Lett* 64:2513–2516
34. Hu YH, Li XF, Wang JJ, Li RY, Sun XL (2013) Free-standing graphene–carbon nanotube hybrid papers used as current collector and binder free anodes for lithium ion batteries. *J Power Sources* 237:41–46
35. Jiang LL, Sheng LZ, Long CL, Fan ZJ (2015) Densely packed graphene nanomesh-carbon nanotube hybrid film for ultra-high volumetric performance supercapacitors. *Nano Energy* 11:471–480
36. Fan W, Miao YE, Huang YP, Tjiu WW, Liu TX (2015) Flexible free-standing 3D porous N-doped graphene–carbon nanotube hybrid paper for high-performance supercapacitors. *RSC Adv* 5:9228–9236
37. Yang Z, Zhao Y, Xiao Q, Zhang Y, Jing L, Yan Y, Sun K (2014) Controllable growth of CNTs on graphene as high-performance electrode material for supercapacitors. *ACS Appl Mater Interfaces* 6:8497–8504
38. Niu JB, Li MT, Xia ZH (2014) Growth mechanisms and mechanical properties of 3D carbon nanotube–graphene junctions: molecular dynamic simulations. *RSC Adv* 4:33848–33854
39. Chen S, Chen P, Wang Y (2011) Carbon nanotubes grown in situ on graphene nanosheets as superior anodes for Li-ion batteries. *Nanoscale* 3:4323–4329
40. Nguyen DD, Tai NH, Chen SY, Chueh YL (2012) Controlled growth of carbon nanotube-graphene hybrid materials for flexible and transparent conductors and electron field emitters. *Nanoscale* 4:632–638

41. Kumar K, Kim Y, Li X, Ding J, Fisher FT, Yang E (2013) Chemical vapor deposition of carbon nanotubes on monolayer graphene substrates: reduced etching via suppressed catalytic hydrogenation using C_2H_4 . *Chem Mater* 25:3874–3879
42. Lim SX, Koon GKW, Zhan D, Shen Z, Özyilmaz B, Sow C (2012) Assembly of suspended graphene on carbon nanotube scaffolds with improved functionalities. *Nano Res* 5:783–795
43. Yu KH, Lu GH, Bo Z, Mao S, Chen JH (2011) Carbon nanotube with chemically bonded graphene leaves for electronic and optoelectronic applications. *J Phys Chem Lett* 2: 1556–1562
44. Lee DH, Kim JE, Han TH, Hwang JW, Jeon S, Choi S, Hong SH, Lee WJ, Ruoff RS, Kim SO (2010) Versatile carbon hybrid films composed of vertical carbon nanotubes grown on mechanically compliant graphene films. *Adv Mater* 22:1247–1252
45. Fan ZJ, Yan J, Zhi LJ, Zhang Q, Wei T, Feng J, Zhang ML, Qian WZ, Wei F (2010) A three-dimensional carbon nanotube/graphene sandwich and its application as electrode in supercapacitors. *Adv Mater* 22:3723–3728
46. Zhang LL, Xiong Z, Zhao XS (2010) Pillaring chemically exfoliated graphene oxide with carbon nanotubes for photocatalytic degradation of dyes under visible light irradiation. *ACS Nano* 4:7030–7036
47. Mao BS, Wen Z, Bo Z, Chang J, Huang X, Chen J (2014) Hierarchical nanohybrids with porous CNT-networks decorated crumpled graphene balls for supercapacitors. *ACS Appl Mater Interfaces* 6:9881–9889
48. Dong XC, Ma YW, Zhu GY, Huang YX, Wang J, Chan-Park MB, Wang LH, Huang W, Chen P (2012) Synthesis of graphene-carbon nanotube hybrid foam and its use as a novel three-dimensional electrode for electrochemical sensing. *J Mater Chem* 22:17044–17048
49. Zhu G, He Z, Chen J, Zhao J, Feng X, Ma Y, Fan Q, Wang L, Huang W (2014) Highly conductive three-dimensional MnO_2 -carbon nanotube-graphene-Ni hybrid foam as a binder-free supercapacitor electrode. *Nanoscale* 6:1079–1085
50. Das S, Seelaboyina R, Verma V, Lahiri I, Hwang JY, Banerjee R, Choi W (2011) Synthesis and characterization of self-organized multilayered graphene-carbon nanotube hybrid films. *J Mater Chem* 21:7289–7295
51. Zhang W, Xie H, Zhang R, Jian M, Wang C, Zheng Q, Wei F, Zhang Y (2015) Synthesis of three-dimensional carbon nanotube/graphene hybrid materials by a two-step chemical vapor deposition process. *Carbon* 86:358–362
52. Jiang J, Li Y, Gao C, Kim ND, Fan X, Wang G, Peng Z, Hauge RH, Tour JM (2016) Growing carbon nanotubes from both sides of graphene. *ACS Appl Mater Interfaces* 8:7356–7362
53. Paul RK, Ghazinejad M, Penchev M, Lin J, Ozkan M, Ozkan CS (2010) Synthesis of a pillared graphene nanostructure: a counterpart of three-dimensional carbon architectures. *Small* 6:2309–2313
54. Dong X, Li B, Wei A, Cao X, Chan-Park MB, Zhang H, Li L, Huang W, Chen P (2011) One-step growth of graphene-carbon nanotube hybrid materials by chemical vapor deposition. *Carbon* 49:2944–2949
55. Zhu X, Ning G, Fan Z, Gao J, Xu C, Qian W, Wei F (2012) One-step synthesis of a graphene-carbon nanotube hybrid decorated by magnetic nanoparticles. *Carbon* 50: 2764–2771
56. Tang C, Zhang Q, Zhao M, Tian G, Wei F (2014) Resilient aligned carbon nanotube/graphene sandwiches for robust mechanical energy storage. *Nano Energy* 7:161–169
57. Tang C, Zhang Q, Zhao M, Huang J, Cheng X, Tian G, Peng H, Wei F (2014) Nitrogen-doped aligned carbon nanotube/graphene sandwiches: facile catalytic growth on bifunctional natural catalysts and their applications as scaffolds for high-rate lithium-sulfur batteries. *Adv Mater* 26:6100–6105
58. Zhao MQ, Liu XF, Zhang Q, Tian GL, Huang JQ, Zhu WC, Wei F (2012) Graphene/single-walled carbon nanotube hybrids: one-step catalytic growth and applications for high-rate Li-S batteries. *ACS Nano* 6:10759–10769
59. Tian GL, Zhao MQ, Yu DS, Kong XY, Huang JQ, Zhang Q, Wei F (2014) Nitrogen-doped graphene/carbon nanotube hybrids: in situ formation on bifunctional catalysts and

- their superior electrocatalytic activity for oxygen evolution/reduction reaction. *Small* 10: 2251–2259
60. Chen T, Zhang Q, Zhao M, Huang J, Tang C, Wei F (2015) Rational recipe for bulk growth of graphene/carbon nanotube hybrids: new insights from in-situ characterization on working catalysts. *Carbon* 95:292–301
 61. Peng H, Huang J, Zhao M, Zhang Q, Cheng X, Liu X, Qian W, Wei F (2014) Nanoarchitected graphene/CNT@porous carbon with extraordinary electrical conductivity and interconnected micro/mesopores for lithium-sulfur batteries. *Adv Funct Mater* 24: 2772–2781
 62. Kosynkin DV, Higginbotham AL, Sinitskii A, Lomeda JR, Dimiev A, Price BK, Tour JM (2009) Longitudinal unzipping of carbon nanotubes to form graphene nanoribbons. *Nature* 458:872–876
 63. Jiao LY, Zhang L, Ding L, Liu J, Dai HJ (2010) Aligned graphene nanoribbons and crossbars from unzipped carbon nanotubes. *Nano Res* 3:387–394
 64. Yang ZB, Liu MK, Zhang C, Tjiu WW, Liu TX, Peng HS (2013) Carbon nanotubes bridged with graphene nanoribbons and their use in high-efficiency dye-sensitized solar cells. *Angew Chem Int Ed* 52:3996–3999
 65. Liu MK, Miao YE, Zhang C, Tjiu WW, Yang ZB, Peng HS, Liu TX (2013) Hierarchical composites of polyaniline-graphene nanoribbons-carbon nanotubes as electrode materials in all-solid-state supercapacitors. *Nanoscale* 5:7312–7320
 66. Liu MK, Miao YE, Zhang C, Tjiu WW, Yang ZB, Peng HS, Liu TX (2013) Hierarchical composites of polyaniline-graphene nanoribbons-carbon nanotubes as electrode materials in all-solid-state supercapacitors. *Nanoscale* 5:7312–7320
 67. Liu MK, Du YF, Miao YE, Ding QW, He SX, Tjiu WW, Pan JS, Liu TX (2015) Anisotropic conductive films based on highly aligned polyimide fibers containing hybrid materials of graphene nanoribbons and carbon nanotubes. *Nanoscale* 7:1037–1046
 68. Liu MK, Zhang C, Tjiu WW, Yang Z, Wang WZ, Liu TX (2013) One-step hybridization of graphene nanoribbons with carbon nanotubes and its strong-yet-ductile thermoplastic polyurethane composites. *Polymer* 54:3124–3130

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