The production of horizontally aligned single-walled carbon nanotubes

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ABSTRACT
The current progress on the production of aligned single-walled carbon nanotubes (SWCNTs), particularly the horizontally aligned ones, is reviewed. There are two main categories for the alignment of SWCNTs: the post synthesis assembly and the in situ growth approaches. The post synthesis assembly approach mainly involves dispersing SWCNTs in solutions and aligning SWCNTs using spin-coating, Langmuir–Blodgett assembly, mechanical shearing, or blown bubble film techniques. The in situ growth approach produces aligned SWCNTs directly during their growth using controlled chemical vapor deposition and arc discharge techniques. The latter approach has the advantage of avoiding the defects generated during the post treatment methods, and may also be combined with other growth controls such as structure selectivity of SWCNTs and direct device patterning for scale up applications.

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1. Introduction

Since the landmark paper on carbon nanotubes (CNTs) by Iijima in 1991 [1], they have attracted widespread attention due to their superior mechanical properties [2], low mass density [3], high electron mobility [4], large current-carrying capability [5], high thermal conductivity [6], and large aspect ratio. These excellent properties of CNTs have made them promising candidates for many applications in the field of nano-electronic devices [7–9], optoelectronic devices [10,11], nanosensors [12,13], transparent and conducting membranes [14,15], and composites [16]. However, the one dimensional character of CNTs leads to extremely anisotropic mechanical, electric, magnetic, and optical properties. Generally, most of their properties along the tube axis are better than that perpendicular to the tube axis orientation. To fulfill these applications, the alignment of CNTs with controlled location and orientation is highly demanded. Alignment can enhance the various properties of CNTs along the alignment orientation. Therefore, aligned CNTs always have better performance than random CNTs. For instance, the best obtained mobility of random single-walled carbon nanotube (SWCNT) networks based thin film transistors (TFTs) was $30 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [17]. In contrast, the mobility of aligned SWCNT arrays based TFTs can reach $1300 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [18].

The main available approaches for the alignment of CNTs can be grouped into two main categories: (a) the post synthesis assembly approaches, which involve dispersing CNTs in solutions, followed by aligning them using spin-coating, Langmuir–Blodgett assembly, mechanical shearing, or blown bubble films technique, and then fixed the aligned CNT structures/patterns by solvent evaporation or resin solidification; and (b) the in situ growth approaches by direct growing aligned CNTs by controlled chemical vapor deposition (CVD) and arc discharge techniques. Several reviews have summarized the studies focused on CNT assemble and characterization [19], as well as direct growth of aligned CNTs by CVD method [20,21]. In the present article, we provide a review of both the post synthesis assembly and in situ growth techniques for controlling the alignment of CNTs, but with the emphasis on the recent developments of horizontally aligned CNTs, particularly on the aligned SWCNTs. The organization of this review is as follows: the first section is dedicated to the post synthesis assembly approaches for the alignment of CNTs; in the second section, the in situ growth of aligned CNTs is surveyed, and finally the last section contains some concluding remarks.

2. Post synthesis assembly approaches

Post synthesis assembly approaches often contain three steps. The first step is dispersing CNTs in solutions. To obtain uniformly dispersed CNT suspensions, CNTs usually need to be treated with chemical functionalization, surfactant encapsulation or polymer/DNA wrapping, and the ultrasonication is often employed. The second step is aligning CNTs by external forces in solutions. The third step is to fix the aligned CNT structures by solvent evaporation or resin solidification. According to their alignment mechanism, post synthesis assembly approaches can be divided into several types as follows.

2.1. Shear introduced alignment

Since CNTs have high aspect ratio, when subjected to shear forces, they will extend straight and align with shear force orientation. The alignment of SWCNTs in polymer solutions has been achieved by shearing SWCNT suspensions with a Brookfield viscometer [22]. Some researchers found that CNTs, like other anisotropic and one-dimensional molecules, could form liquid crystal phases when they were highly concentrated in solutions [23–26]. Such liquid crystal phase contains some self-aligned CNT fragment. However, the alignment lengths are only a few micrometers. Anglaret and co-workers used denaturized DNA to disperse SWCNTs and form lyotropic nematic phases. Two methods, linear shearing and spin-coating (Fig. 1(a)) were employed to mechanically shear lyotropic nematic SWCNT aqueous suspensions, and both of these two processes were effective on preparing homogeneous anisotropic thin films of aligned SWCNTs [27]. But the alignment of SWCNTs in films seems weak as revealed by polarized Raman spectra and scanning electron microscope (SEM) (Fig. 1(b) and (c)). More recently, Lu and Chen reported the fabrication of well aligned SWCNT films by mechanical shearing of SWCNT liquid crystal [28]. It is suggested that the removal of spherical impurities from SWCNTs is very important for achieving well alignment of SWCNTs. By spin-coating SWCNT/N-methyl-2-pyrrolidinone solutions with high spin rate, Bao and co-workers prepared density and aligned SWCNT films on organic molecule modified silicon wafers [29,30]. In addition, they also achieved semiconducting and metallic SWCNT selective sorting on different organic molecule functionalized silicon surfaces.

Generally, the shear introduced alignment of CNTs always performed in solutions. Recent work by Homma and co-workers showed that this method could also be applied in "dry" process [31]. They used contact printing process to transfer random SWCNT films grown on SiO$_2$ onto another surface (Fig. 1(d)). When the growth substrate was slid over the receiver substrate during the transfer process, these random SWCNTs could form high density and horizontally aligned SWCNT arrays on the receive substrate (Fig. 1(e)).

2.2. Flow directed alignment

Flow directed alignment process provides an effective way to align CNTs [32–36]. As mentioned in Section 2.1, CNTs might form liquid crystal phase when in concentrated CNT
Fig. 1 – (a) Scheme of approaches for aligning lyotropic nematic phases by mechanical shearing: liner shearing (top) and spin-coating (down). (b) Polarized Raman G band spectra and (c) Typical SEM image of aligned SWCNT film obtained by mechanical shearing. (d) Schematic diagram of the transfer and alignment of SWCNTs. (e) SEM image of aligned SWCNT arrays on SiO$_2$ substrates prepared by contact printing. Source: (a–c): Reproduced with permission from [27]. Copyright 2008 American Chemical Society. (d & e): Reproduced with permission from [31]. Copyright 2010 American Chemical Society.

Fig. 2 – (a) Schemes for the tilted-drop fabrication of a thin film on an amine-terminated SAM surface micro-patterned with photoresist polymer stripes. (b) AFM topographical images of carbon nanotube films showing uniaxially oriented, densely packed CNT bundles. (c) Hydrodynamics in a cylindrical drop to align and place anisotropic nanoparticles. (d) AFM topographic images showing alignment and placement of individual SWCNT along the edges of the polar SAM (ovals highlight SWCNT). Source: (a & b): Reproduced with permission from [39]. Copyright 2006 American Chemical Society. (c & d): Reproduced with permission from [42]. Copyright 2007 American Chemical Society.
solutions. They can further assemble into long range aligned CNT arrays by fluidic flow [37–39]. A successful example was reported by Ko and Tsukruk [39], which dropped SWCNT aqueous solution on a tilted NH2-terminated self-assemble monolayer (SAM) surface with photoset polymer stripes (Fig. 2(a)). SWCNT solutions assembled on the hydrophilic microchannels and formed confined micro-patterned geometry. As the solvent evaporating, SWCNTs concentrated at the liquid–solid–air receding contact line and formed a nematic liquid crystal phase. Because the substrate was tilted, the drying process also caused a unidirectional microfluidic flow to align the SWCNTs and formed aligned SWCNT arrays (Fig. 2(b)). Windle and co-workers reported the study of the drying process of SWCNT aqueous suspension on substrates [37]. Aligned SWCNT geometry was observed on the edge of the dried SWCNT drops. They attributed the driving force for orientation of SWCNTs to the minimized energy in the splay field induced by the acute angle between the solid–liquid–vapor interfaces.

There are two modes for the evaporation of drops on solid surfaces. One is depinned contact or shrinking, in which the contact angle remains constant and the contact area decreases during drops evaporation. The second mode is pinned contact, in which the contact area is constant with decreasing contact angle [34]. If a droplet of colloidal suspensions evaporation follows pinned contact mode, the solid–liquid–vapor interface (contact line) of the drying droplet is pinned, and the liquid evaporating from the edges is replenished by liquid from the interior. This leads to an internal flow toward the contact line. The internal flow carries the suspended particles toward the edges of the droplet and forms ring-shaped deposition. This is the so called “coffee ring” phenomenon [33,40,41]. Strano and co-workers used this phenomenon in evaporating micrometer scale high aspect ratio cylindrical droplets to achieve the alignment of SWCNTs [42]. The cylindrical droplets of SWCNT aqueous solutions were formed on a patterned gold surface with alternating rectangular stripes of polar and non-polar SAMs. After the solvent evaporating, SWCNTs aligned with the patterned stripes and were placed in the edge of polar region by the hydrodynamic flow (Fig. 2(c) and (d)). In their subsequent work, they found that when the width of the polar stripes was reduced below 1 μm, the drying mode would switch to depinned contact, therefore the hydrodynamic flow reversed toward the center-line of droplets and formed aligned SWCNTs in the center of polar region [43]. Similarly, using "coffee ring" phenomenon and nematic liquid crystal behavior of SWCNT solutions, Avouris and co-workers prepared micro-wide strips with arrays of dense and aligned SWCNTs [44].

2.3. Electric field directed alignment

Since the static polarizability tensor ε of a CNT is highly anisotropic, the polarizability along the tube axis is much higher than that perpendicular to the tube axis [45]. An applied electric field will introduce large dipole moments and lead to large aligning torques that forces CNTs aligning to electric field orientation. Chen et al. prepared aligned SWCNTs in a 25 μm gap between two golden electrodes by applying an alternating current (ac) electric field with frequency of 5 MHz and a magnitude of 10 V peak to peak [46]. Kamat et al. developed an electrophoretic deposition method for the alignment of SWCNTs in a direct current (dc) electric field [47]. SWCNTs were suspended in tetrahydrofuran (THF) solution with the assistant of tetraoctylammonium bromide (TOAB). When a higher dc electric field (>100 V) was applied, the quaternary ammonium capped SWCNTs assembled as stretched bundles and aligned perpendicular to the electrode surface. The electric field directed assembly technique can also be used to align CNTs in polymer matrix to prepare CNT enhanced composites with anisotropic properties [48,49].

Another approach for CNTs aligning by electric field is dielectrophoresis [50–53]. Since metallic and semiconducting SWCNTs have different dielectric constants, SWCNTs can align while separately deposited on different area by electronic type (semiconducting or metallic) in an ac dielectrophoretic process. This feature makes ac dielectrophoresis an efficient way for separating and sorting metallic and semiconducting SWCNTs [54,55].

2.4. Magnetic field directed alignment

Orientation of diamagnetic molecules in the presence of a magnetic field is a well-known phenomenon for organized structures. It is predicted that both semiconducting and metallic SWCNTs exhibit anisotropic magnetic susceptibility in parallel and perpendicular to tube axes [56,57]. When SWCNTs placed in a magnetic field, they will acquire extra anisotropic magnetic energy and a torque is created that make them aligned parallel to the applied magnetic field to minimize the magnetic energy. When this anisotropic magnetic energy overcomes the randomizing thermal motion (Brownian motion) energy, SWCNT alignment can be achieved [58]. For an individual (10, 10) SWCNT of length 300 nm, the predicted magnetic field is 15.3 T to achieve alignment at room temperature [58]. Several works have been done for the alignment of both SWCNTs and multi-walled carbon nanotubes (MWCNTs) in strong magnetic field [58–61]. For example, Walters et al. prepared aligned membrane of SWCNTs by filtering SWCNT suspensions in strong magnetic field [58]. SWCNTs were first dispersed in Triton-X suspension, and then the SWCNT suspensions were filtered in a 25 T parallel magnetic field, which cause SWCNTs aligned within the magnetic field. Finally, aligned SWCNTs deposited on filters and form in-plan-aligned membranes. Ago and co-workers reported a method to prepare anisotropic MWCNTs-polymer composites [61]. In their approach, MWCNTs were aligned in monomer solution of unsaturated polyester under a 10 T magnetic field, and then polymerizing the monomer matrix to freeze the alignment of MWCNTs. Similarly, Chio et al. prepared aligned SWCNT-epoxy composites by hardening the SWCNT-epoxy resin in a 25 T magnetic field [59].

Due to the weak anisotropic magnetic susceptibility of CNTs, it has to apply very strong magnetic fields (tens of Tesla) for their alignment. However, it is possible to align CNTs in a weak magnetic field when CNTs coated with ferromagnetic materials [62]. Correa-Duarte et al. demonstrated that the alignment of MWCNTs could be achieved in a 0.2 T magnetic field through deposition of uniform layers of γ-Fe2O3/Fe3O4 nanoparticles [63]. Using similar strategy, Jung
and co-workers developed a magneto-evaporation method for fabricating vertical aligned SWCNT structures [64]. They first fabricated Fe-oxide/SWCNT samples, and then the Fe-oxide/SWCNT samples were dispersed in N,N-dimethylformamide and the resulting solution was deposited on an ITO glass substrate using the spraying method with magnetic field. After evaporation of the SWCNT solution in the presence of a magnetic field, the nanotubes were transferred to the vacuum-evaporator chamber, and titanium was evaporated by e-beam evaporation to hold the vertical alignment of the SWCNTs.

2.5. Blown bubble film

Blown film extrusion is widely used for the manufacture of plastic films in large quantities. Yu et al. extended this technique to fabricate composite films of aligned CNTs [65]. As illustrated in Fig. 3(a), SWCNTs and MWCNTs were firstly functionalized with n-octadecylamine (ODA). The ODA functionalized SWCNTs/MWCNTs were then dispersed in THF to obtain different wt.% solutions. The epoxy resin and hardener were subsequently added to CNTs/THF solutions and yield a homogeneous, stable and controlled concentration polymer suspension of CNTs. Then, the polymer suspension was expanded using a circular die to form a bubble at controlled pressure. Finally, the bubble film was transferred to substrates or open frame structures. These bubble films contained uniformly aligned and controlled-density CNTs (Fig. 3(b)). The blown-bubble films with aligned CNTs could be transferred to different substrates, such as single-crystal wafers of at least 200 mm in diameter, flexible plastics sheets of dimensions of at least 225 x 300 mm$^2$ and highly curved surfaces. Recently, Benattar and co-workers reported a bubble-deposition method for the formation of aligned SWCNT monolayer [66]. SWCNTs were first dispersed in water solution by adding sodium dodecyl benzene sulfonate (SDBS). The bubble of SWCNT suspension was formed in controlled humidity condition and in the absence of vibrations. These bubbled films could be transferred onto hydrophobic substrates and form high density and aligned SWCNT geometries (Fig. 3(c)). However, as the authors pointed out, the prepared aligned SWCNT film was not uniform: the regions far away from the center were highly aligned (Fig. 3(d)), while in the center of the film, the SWCNTs were randomly oriented (Fig. 3(e)).

2.6. Langmuir–Blodgett assemble

Langmuir–Blodgett (LB) assemble technique is an efficient way to fabricate monolayers of aligned one-dimensional nanowires and nanotubes [67–70]. The scheme of LB alignment is shown in Fig. 4(a). Usually, nanotubes are wrapped
or covalently functionalized with macromolecules to solubilize CNTs in organic solvent and ensure them floating on the water surface. When floating CNTs are compressed with computer-controlled trough barriers, CNTs reorient themselves and align parallel to the trough barrier, forming a closely packed monolayer. This floating monolayer of aligned CNTs can then be transferred onto substrates. Dai and co-workers have reported the preparing of aligned monolayers of PmPV noncovalently functionalized SWCNTs with dense packing on SiO2 substrate by LB method (Fig. 4(b)) [67]. Combined with microcontact printing, LB method also can be used to prepare patterned and hierarchically aligned SWCNT structures[71].

Post synthesis assemble approaches provide the ways to purify or sort CNTs before alignment, and most of these techniques can be operated at room temperature. However, the CNT dispersing process, which requires chemical functionalization and ultrasonication, always creates wall defects and deteriorates the intrinsic properties of CNTs.

3. In-situ growth approaches

The study of in situ growth of aligned CNTs originated from directly growing of vertical aligned MWCNTs (MWCNT forest) [72]. Several groups have reported the growing of both SWCNT and MWCNT forests [73–79]. The important innovation on in situ growth of vertically aligned CNTs is the water-assisted CVD growth, also called “supergrowth”, which can produce dense CNT forests with millimeter-scale height [74]. Recently, Hata and co-workers have reported the synthesis of 1 cm tall SWCNT forest with 1 x 1 cm size by controlling the gas flow direction in water-assisted CVD process, and they also obtained SWCNT forest with area up to A4 size (210 x 297 mm) [80]. In the following, we will focus on the techniques for horizontal aligned CNTs.

3.1. Electric field directed CVD

As mentioned earlier, the alignment of CNTs in solution can be achieved by applying electric field. Similarly, this electric field directed alignment strategy can also be applied in the CVD synthetic process. For example, Dai and co-workers prepared aligned SWCNTs by introducing an external electric field during a CVD process. These aligned SWCNTs across over the trenches between the electrodes with poly-Si and Mo [81,82]. A key of the alignment growth of SWCNTs is that the SWCNTs should suspend in air during growth to keep SWCNTs from van der Waals interactions with nearby surfaces. This is because if SWCNTs contact the substrate, strong van der Waals interactions with the substrate will hold SWCNTs in place and prevent its response to the electric field. Similarly, Joselevich and Lieber reported the vertical growth of SWCNT arrays by electric field directed CVD growth from patterned catalyst nanoparticles [83].

3.2. Gas-flow-directed CVD growth

Conventional CVD process on flat substrates usually produces randomly oriented SWCNTs, probably because the strong van de Waals interaction between catalyst nanoparticles and substrate may hinder the alignment of SWCNTs during growth and even poison the catalyst. Liu and co-workers developed a “fast heating” CVD technique to achieve the growth of long and aligned SWCNTs on silica/silicon surfaces by using Fe–Mo nanoparticles as catalysts and CO as feeding gas (Fig. 5a) [84]. The SWCNTs grew along the gas flow direction and their length can be over 2 mm. They believed that the “fast heating” which leads a quick growth of SWCNTs at the initial stage ensured SWCNTs sliding along the substrate without strong interaction with the substrate. This method can also be used to directly grow two-dimensional crossed-network of SWCNTs by a two-step growth process (Fig. 5(b)). In subsequent work, they proposed a “kite mechanism” to explain the growth of aligned SWCNTs by “fast heating” CVD process [85]. As shown in Fig. 5(c), at the initial “fast heating” CVD process, the fast heating led to the temperature difference between solid sample and the surrounding gas due to their different heating speed. The temperature difference may generate a convection flow which can lift some of nanotubes up with the catalysts on their tips. During the growth stage, the catalysts at the SWCNT end were floating like a kite and laminar flow dominated the growth orientation of SWCNTs. Because catalysts were floating above the substrates, the strong van de Walls interaction between catalysts and substrate was eliminated, which ensured easily controlling the SWCNT orientation by gas flow. Using similar strategy, Li and co-workers synthesised horizontally aligned SWCNT arrays on silicon wafers with Cu as catalyst and
methane as feeding gas [86]. The length of SWCNTs can be up to a centimeter and the density of the arrays can reach 2–3 SWCNTs/10 μm (Fig. 5(d)). In addition, they also found that the horizontally aligned SWCNTs can be prepared without fast heating when using ethanol as carbon sources. They attributed the growth of ultralong aligned SWCNTs to the weak interaction between the copper catalysts and silica surfaces.

The laminar flow-assisted technique is another successful strategy for the growth of aligned CNTs. It is accepted that a stable laminar gas flow, which facilitate to stabilize the catalysts at the end of growing CNTs and make the catalysts travel long distances, plays a key role in the growth of long and aligned CNTs [87]. The stability of the gas can be estimated by the Reynolds number \( Re = \frac{\rho v d}{\gamma} \), where \( \rho \) is the density of gas mixture, \( v \) is the flow speed, \( d \) is the furnace tube diameter, and \( \gamma \) is gas coefficient viscosity. To grow aligned CNTs, the flow should be controlled as laminar flow (\( Re < 2000 \)) [21]. When \( Re > 2000 \), the flow is unstable turbulent flow and can’t support the growth of aligned CNTs. Several groups have achieved the growth of aligned CNTs by tailoring the Reynolds number [87–90]. Kim and co-workers designed a tube-in-tube structure to reduce the diameter-dependent Reynolds number [87]. Using Fe as catalysts and CH₄/H₂ as feeding gas, they successfully synthesised aligned and ultralong MWCNT/SWCNTs on the SiO₂ substrates. The length of MWCNTs grown in this process was up to 10 cm. Li and co-workers prepared aligned SWCNT arrays under extremely low feeding flow of 1.5 sccm in a 1 inch quartz tube reactor [89]. They suggested that the buoyant effect of convection flow arising from the vertical gradient of gas temperature and density can lift the catalyst particles and the growing SWCNT away from the substrate. And both the low flow rate and small quartz tube diameter benefit the reducing of the Re value and stabilizing the laminar flow to ensure the alignment of SWCNTs.

The fact that the catalyst nanoparticles are floating above the substrates during CNT growing is believed to facilitate the elongation of the lifetime of the catalysts and grow CNTs with high rate. Therefore, the gas-flow-directed CVD growth is an ideal way to grow ultralong SWCNTs and MWCNTs. The growth of aligned ultralong SWCNTs over 18.5 cm on Si substrates was reported by Li and co-workers [91]. The growth rate of the SWCNTs was more than 40 μm/s. Recently, Wei et al. reported the growth of 20 cm long double-walled CNTs and triple-walled CNTs at a rapid growth rate of 80–90 μm/s by a gas flow directed CH₄–H₂O CVD process [92]. The adding of small amount of water was believed to remove the amorphous carbon on the active metal catalyst surface and maintain the catalyst activity.

![Fig. 5](image-url)
3.3. Surface-lattice-guided CVD growth

In general, to grow aligned SWCNTs on substrate, the SWCNTs should grow above the surface because strong van der Waals interactions between the SWCNTs and substrates may hinder the smooth growth of SWCNTs. However, several studies demonstrated that surface interactions between SWCNTs and single crystal substrates with anisotropic lattices or miscut atomic steps could enable the growth of parallel aligned SWCNTs. The first report about the control of CNT orientation using a single crystal substrate came from Liu’s group [93], where an oriented growth of SWCNTs on silicon surface due to the different interaction of SWCNTs with different lattice was achieved. Joselevich and co-workers reported that aligned SWCNTs could grow along 0.2 nm high atomic steps on a miscut c-plane sapphire surface (Fig. 6(a) and (b)) [94]. In their subsequent work, the sapphire substrates were annealed in air at 1100 °C before CVD growth, and 1.3 nm high faceted nanosteps were generated on miscut c-plane sapphire surface, which was then served as templates for the growth of highly aligned SWCNTs [95]. Recently, the aligned growth of SWCNTs on SiO$_2$/Si was achieved by creating V-shaped trenches on Si (1 0 0) through anisotropic etching [96]. Without the nanostep template,
Zhou and co-workers succeeded in growth of parallel aligned SWCNTs on α- and r-plane sapphire substrates [97]. In contrast, they only got randomly orientated SWCNTs on c- and m-plane. They believed that the catalyst-substrate interaction was the main reason for the directional growth of SWCNTs on special crystal plane of sapphire. Beside the orientation, the diameter and chirality of SWCNTs are affected by crystal plane of the sapphire substrate. Ago and co-workers investigated the SWCNT growth on different crystal planes of sapphire by photoluminescence and resonant Raman spectra. The results revealed that the SWCNT growing on α- and r-planes of sapphire had narrower diameter distributions than randomly oriented tubes produced on the c-plane sapphire. In addition, near-zigzag SWCNTs were observed on the α-plane and near-armchair SWCNTs on the r-plane [98]. The mechanism of horizontally aligned growth of SWCNTs on r-plane sapphire was investigated by Yu et al. [99]. They suggested that the anisotropic interaction between Al atoms in the [110] direction on the oxygen-depleted sapphire and SWCNTs was responsible for the alignment in the middle part of the wafers while atomic steps or nanosteps played a key role for aligned growth of SWCNTs at the edges of the wafers.

The surface-lattice-guide CVD growth can also performed on some specific cutting treated single-crystal quartz surfaces. Rogers and co-workers obtained large-scale and horizontally aligned arrays of SWCNTs on the annealed AT-cut single-crystal quartz substrate [100]. AFM images showed that steps with 0.7–1.0 nm high and 30–35 nm spacing appeared on AT-cut single-crystal quartz surface after thermal annealing at 900 °C. They believed such steps guided the alignment of SWCNT growth. Increasing the annealing time, SWCNT alignment can be improved due to the increase of the degree of order in the crystal lattice as well as the lengths and order of the steps. In 2008, Liu and co-workers reported the synthesis of high density and perfectly aligned arrays of long SWCNTs on stable temperature (ST)-cut quartz substrates using copper as catalyst and ethanol as carbon source (Fig. 6(c)) [101]. The density can reach >50 nanotubes per micron and the length can be a few millimeters (Fig. 6(d)). In their subsequent work, selective growth of aligned semiconducting SWCNTs was achieved by introducing methanol in the growth process [102]. Recently, Rogers and co-workers developed a sequential CVD method that involves multiple and separated CVD growth cycles to improve the density of aligned SWCNTs on ST-cut single crystal quartz substrates [103]. It was found that the densities reached values of 20–30 SWCNTs μm⁻¹ uniformly over the double-grown areas, which were 1.5–2 times higher than in single-grown areas.

Combined with other aligned growth techniques, the surface-lattice-guided CVD growth can be used to build complex nanotubes structures. Three-dimensional (3D) structures with vertical nanotube forests and horizontal nanotube
arrays were selectively synthesised by delicately controlling CVD conditions (Fig. 6(e)) [104]. Combined with the gas flow directed CVD, the “nanotube serpentine” were fabricated on quartz substrates (Fig. 6(f)) [105]. The surface-lattice-guide CVD growth provided an efficient way to synthesise high density parallel aligned SWCNTs. Since the aligned growth of SWCNTs is highly dependent on the surface interactions between SWCNTs and single crystal substrates, it is hard to grow aligned SWCNTs with multi layers. In addition, the common notable drawback of CVD methods is that SWCNTs can only grow on some selective substrates and the direct growth of aligned SWCNTs on flexible substrates such as plastics is impossible due to the high temperature process (500–900 °C) for the synthesis of SWCNTs.

3.4. Magnetic field assisted electric arc discharge growth

The electric arc discharge method is known as one of the most efficient techniques for large-scale synthesis of SWCNTs, which have fewer defects and narrower diameter distribution than those produced by low temperature CVD techniques [106]. Recently, we have extended this technique to in situ preparing of aligned SWCNT films by adding a low magnetic field (see Fig. 7a) [107]. This approach can be described as a combined in situ evaporation and coating process. In this process, the in situ generated SWCNT aerosol was applied with a much weaker magnetic field (0.56 T) during the SWCNT aerosol diffusion to the substrates. Thus, the SWCNTs were aligned along the magnetic field orientation due to their anisotropic magnetic susceptibility nature (Fig. 7b). It is believed that the SWCNTs dispersed in low viscous helium gas and the long bundle nature of arc discharge synthesised SWCNTs were the main reasons for SWCNT alignment in such a low magnetic field. Since the orientation of aligned SWCNT film is only determined by the relative direction between applied magnetic field and substrate, the alignment orientation of SWCNTs can be easily changed by rotating the substrate. Therefore, multiple layers structure where each layer has different orientation and location can be fabricated simply by adjusting the orientation and position of the substrate/mask. Since one practical challenge for direct growth of aligned SWCNT film is selection of the substrates, which need to standard the typical high temperature, the in situ growth of aligned SWCNTs using a rather weak magnetic field in arc discharge demonstrated that we now do not have such limitation and further more, various substrates such as flexible and organic substrates can be used for 2-D and 3-D aligned SWCNT nano structures (Fig. 7c).

4. Summary

We have provided an overview of the recent progress on CNT, particularly horizontally aligned SWCNTs. The two main approaches for CNT alignment or/and orientation include the post synthesis assembly and the in situ growth methods. Among the methods using the post synthesis approach, in some cases they are relatively simple, but in most cases they have the serious disadvantages for causing more defects and external materials such as surfactants have to be used. Rather, the in situ growth approach could avoid such problems, which could combine with some patterning technologies. Importantly, most of advanced applications of CNT require both such alignment/orientation and CNT uniform with desired diameter and chirality. While some great progress has been made for the latter issue, its combination with the alignment/orientation still needs much more effort for real applications of CNTs. For the alignment/orientation issue, great challenges still remain. First, it is still hard to fabricate aligned CNTs with controlled density by current techniques. Second, techniques are still required for scalable and large scale preparation of aligned CNTs over a large area. Overall, for many prospective applications of CNT, the most important challenge is believed to achieve both the alignment and homogeneous electronic structure (all semiconducting or all metallic, or even with uniform diameter and chirality) all together with the capability to scale up.

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