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Carbon Nanotube-Activated Thin Film Transparent Conductor Applications

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Abstract

Carbon nanotubes are an exciting nanomaterial system that exhibit exceptional mechanical and electrical properties. Due to its small diameter of ~ 1 nm and high aspect ratio in order of 10^3 , they can readily form interconnected conducting network of continuous film with high transparency. Transparent conductor based on carbon nanotube can be grown directly into a thin-film structure, or can be processed after the growth process. Post-growth arrangement of carbon nanotube into transparent conducting thin films can be achieved by several methods. Most of the methods involve solution-processed approach, while dry-processed approach is also possible. This chapter presents a comprehensive review and methods for fabricating transparent carbon nanotube-activated thin film, which generally demonstrate high conductivity and mechanical flexibility. Comparison on the optical and electrical performance of the carbon nanotube-activated transparent conductors fabricated via different methods is presented in the chapter.

Keywords: carbon nanotube, transparent, conductor, thin films, fabrication, methods

1. Introduction

The advent of mobile and interactive devices has seen tremendous increase in demand for transparent conductors. The commonly used material as transparent conductor such as indium tin oxide (ITO) is scarce, expensive, brittle and suffers from thermal-related degradation. There is a need for alternative material system which is cheaper and readily available to complement or even replace ITO in the future. Such a material system is carbon nanotube-activated thin film transparent conductor.

Carbon nanotube-activated thin film transparent conductor exhibits excellent electrical conductance, high carrier mobility, high flexibility, and environmental robustness. Furthermore, coupled with a variety of simple fabrication methods, this material is suitable for emerging technology applications such as photovoltaic electrodes, organic light emitting diodes (OLEDs), touch panels, field emitters, smart windows, and smart fabrics. The easiest route for fabricating carbon nanotube-activated thin film transparent conductor is via simple spin-coating method.

Recent work utilizing the multi-walled carbon nanotubes has shown to reduce sheet resistance via nanotube length optimization [1]. Double-walled carbon nanotubes can also be used to produce the thin film transparent conductors via dip coating method and has been shown to be superior to that of multi-walled carbon nanotubes with low sheet resistance of $\sim 134 \Omega/\square$ or lower and 99% transmittance at 550 nm [2]. Single-walled carbon nanotubes activated transparent conducting films on the other hand can be further doped with HAuCl_4 to enhance the optoelectronic performance of $\sim 40 \Omega/\square$ sheet resistance and $\sim 90\%$ transmittance [3].

A successful demonstration of carbon nanotube-activated thin film transparent conductor as a strain sensor application showed high sensing range of up to 400% and fast response of less than ~ 98 ms with a transmittance of 80% at 550 nm [4]. The performance of carbon nanotube-activated thin film is also comparable to graphene-activated thin film. A recent demonstration of inverted perovskite solar cell application of carbon nanotube- versus graphene-activated thin film showed a power conversion efficiency of 12.8 and 14.2%, respectively [5]. It is also possible to integrate both carbon nanotube and graphene in a hybrid structure as the thin film to further enhance the optoelectronic and mechanical performances [6].

In this chapter, the basic theoretical background of carbon nanotubes is briefly explored, followed by their application as transparent conductors. In the following section, an in-depth discussion of selected transparent film fabrication methods such as dip coating, vacuum filtration, and Langmuir-Blodgett is carried out. The optical and electrical performances of films fabricated by the different fabrication methods are also compared.

2. Carbon nanotubes

2.1. Carbon nanotube properties

Carbon nanotube (CNT) is a type of carbon allotrope, also referred to as nanoallotropes due to their nanometer dimensions. It belongs to a graphemic nanostructure group consisting of densely packed hexagonal honeycomb sp^2 carbon crystal lattice, similar to graphene. CNTs structurally are hollowed tubular cylinder with wall made up of a hexagonal carbon honeycomb with a very high aspect ratio in order of thousands.

A single-walled carbon nanotube (SWCNT) is a type of CNT with a wall consisting of a single atomic layer of carbon atoms bonded together in a hexagonal honeycomb structure. It can be imagined as a monolayer of graphene rolled into a capped cylinder. However, the synthesis

method is not as straightforward. Depending on the orientation of the rolling axis of the graphene layer, SWCNTs exhibit varying electronic properties, that is, varying bandgap and also varying diameter in the range of 0.7–3.0 nm. This varying tube properties, or species, based on the varying rolling axis orientation is denoted by the chiral number (n, m) . Therefore, SWCNTs can be tuned to exhibit electronic properties that of metallic elements (conducting) or semiconducting with varying bandgap based on its chirality. Studies have shown that an (n, m) tube is metallic when $n = m$, or when $n - m = 3i$, where i is an integer, while semiconducting CNTs have $n - m \neq 3i$ [7].

Figure 1 shows examples of SWCNT structures. A zigzag SWCNT is a species when $m = 0$, an armchair SWCNT is a species, when $n = m$, and a chiral SWCNT is a species with any other combination of (n, m) . A multi-walled carbon nanotube (MWCNT) is another type of CNT with a stack of multiple graphene layers forming the wall structure in a concentric fashion similar to a Russian doll. MWCNTs can have a diameter anywhere in the range of 3–20 nm. Theoretically, tube diameter in the excess of 100 nm is possible for MWCNT. CNTs exhibit extraordinary mechanical and electrical properties for a 1D quantum wire. In particular, CNTs have high electrical conductivity ($\rho \approx 10^{-6} \Omega \text{ m}$) [8]. This high conductivity arises from the confinement of electrons, which allows one dimensional (1-D) electron movement in either direction along a single line and the requirements for energy and momentum conservation, resulting in reduced scattering processes [9]. Theoretically, in the absence of scattering, transport is ballistic with unit conductance $G = 2e^2/h$ with the resistance of 12.9 k Ω [10]. CNTs also have high thermal conductivity ($k = 1750\text{--}58,000 \text{ W/mK}$) [11], high tensile strength (60 GPa) [12], and

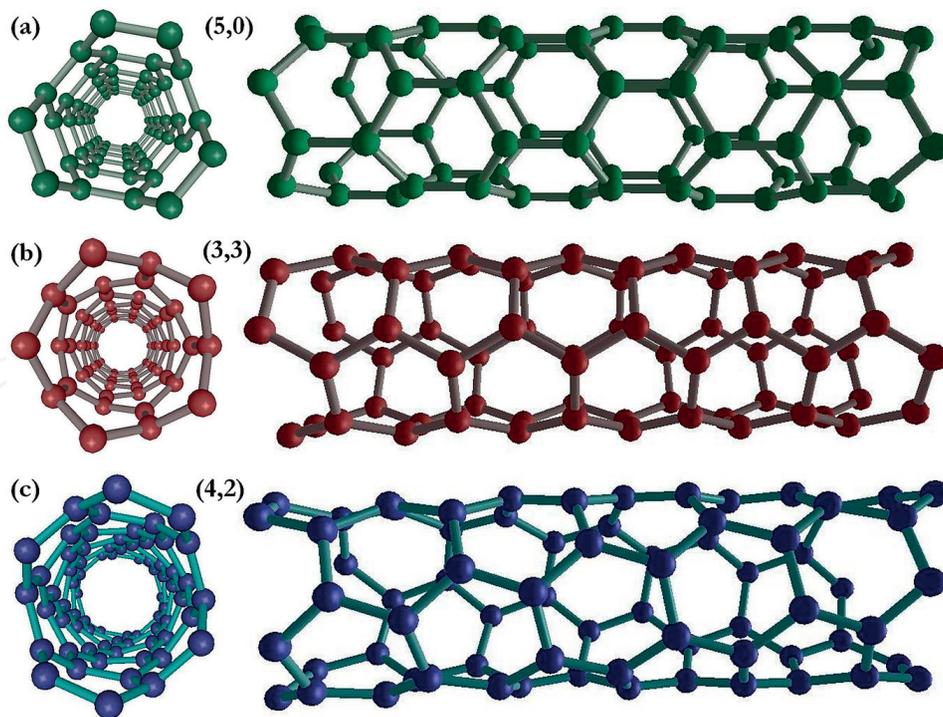


Figure 1. Graphical representation of different SWCNT physical structures from the front (left) and side perspectives (right). (a) A zigzag SWCNT with chiral number (5,0). (b) An armchair SWCNT with chiral number (3,3). (c) A chiral SWCNT with chiral number (4,2).

high Young's modulus (1 TPa) [13]. The closed structure at the edges and no dangling bonds in CNTs makes them chemically stable and inert. The C atoms in CNTs are completely covalently bonded, and therefore do not suffer from electromigration or atomic diffusion like metals, making them a very good electrical conductor that can sustain high current densities ($>10^9$ A/cm²) [14, 15]. All these properties make CNTs one of few materials that have very good prospects of driving technology progress in future electronics and other applications.

Most of the applications of CNTs are due to its mechanical resilience and ballistic electric conductivity. The vast applications of CNTs are evident with different new findings being reported continually over the last two decades. In electronics, the most important applications are carbon nanotube field effect transistors (CNTFET), circuit interconnects, and transparent conducting films. New studies of CNTFETs led to many findings of its new uses; CNT power transistors, biosensors, electromagnetic wave sensors, gas sensors, memory elements, and transparent flat devices are some of the possible applications derived from a basic CNTFET operation.

Currently, the popular methods of mass producing CNTs are arc discharge, laser ablation, and chemical vapor deposition (CVD). Ebbesen and Ajayan in 1992 managed to demonstrate the growth and purification of MWCNT with high quality and quantity (gram level) by arc discharge [16]. Arc discharge technique involves generating an electric arc between two graphite electrodes with one of them filled with catalyst metal powder such as Fe, Ni, and Co, in a He gas atmosphere. In the laser ablation method, a laser is used to evaporate a graphite target that is mixed with catalyst powder [8]. Both arc discharge and laser ablation methods produce only up to 70% CNTs, while the rest are amorphous carbon and catalyst particles, making it necessary to carry out a post-growth purification step. The CVD process uses catalyst metal nanoparticles reacted in hydrocarbon gas at temperatures of 450–1100°C [17]. The catalyst nanoparticles will decompose and dissolve the hydrocarbon gas before precipitating out from its circumference as CNT [18]. Recently, the CVD method has gained much popularity because of the ability to control the morphology and the quality of the CNT that sparked different variants of the CVD methods such as plasma enhanced CVD (PE CVD) [19], high-pressure catalytic decomposition of carbon monoxide (HiPCO) [20], Co-MoCat process [21], and alcohol CVD [22].

2.2. Carbon nanotubes as transparent conductors

A lot of study has been done in applying CNTs as materials for transparent conductors [23]. The key advantages of CNT as transparent conductor relate to their outstanding structure and electronic properties. Structurally, CNTs have extremely small diameters of ~ 1 nm and high aspect ratio in the order of 10^3 , making them readily to form intercalating assembly of continuous tube network as thin as a few nanometers. Being mechanically strong and flexible, a thickness of a few nanometers is enough to mechanically manipulate them into device structures. Electronically, CNTs show outstanding conductivity and current carrying capacity up to 1000 times better than Cu. Combining these two characteristics of CNT films, they are suitable and exciting material system for application in technologically relevant electronic devices

requiring high conductivity and transparency toward visible light electromagnetic radiation and beyond.

Furthermore, SWCNTs can be metallic or semiconducting based on its chirality. Normally, synthesized SWCNTs will contain statistically a mixture of both types of tube with the ratio of metallic to semiconducting tube to be 1–3, approximately [9]. Ideally, transparent conducting films based on SWCNTs require tube composition of totally metallic tubes to maximize the total conductivity. Efforts to grow selectively metallic or semiconducting SWCNTs have remained as the holy grail of CNT electronics and have been carried out rigorously over last decade. It is possible to selectively enrich the growth of metallic [24] or semiconducting [25] SWCNTs. However, obtaining 100% selectivity is still not possible or at least still cannot be completely verified due to the limitations of the characterization methods available. In addition, selective growth of SWCNTs also requires specific growth platform or substrate, such as specifically oriented quartz substrates, which can pose additional problem in transferring and processing the tubes into thin transparent films.

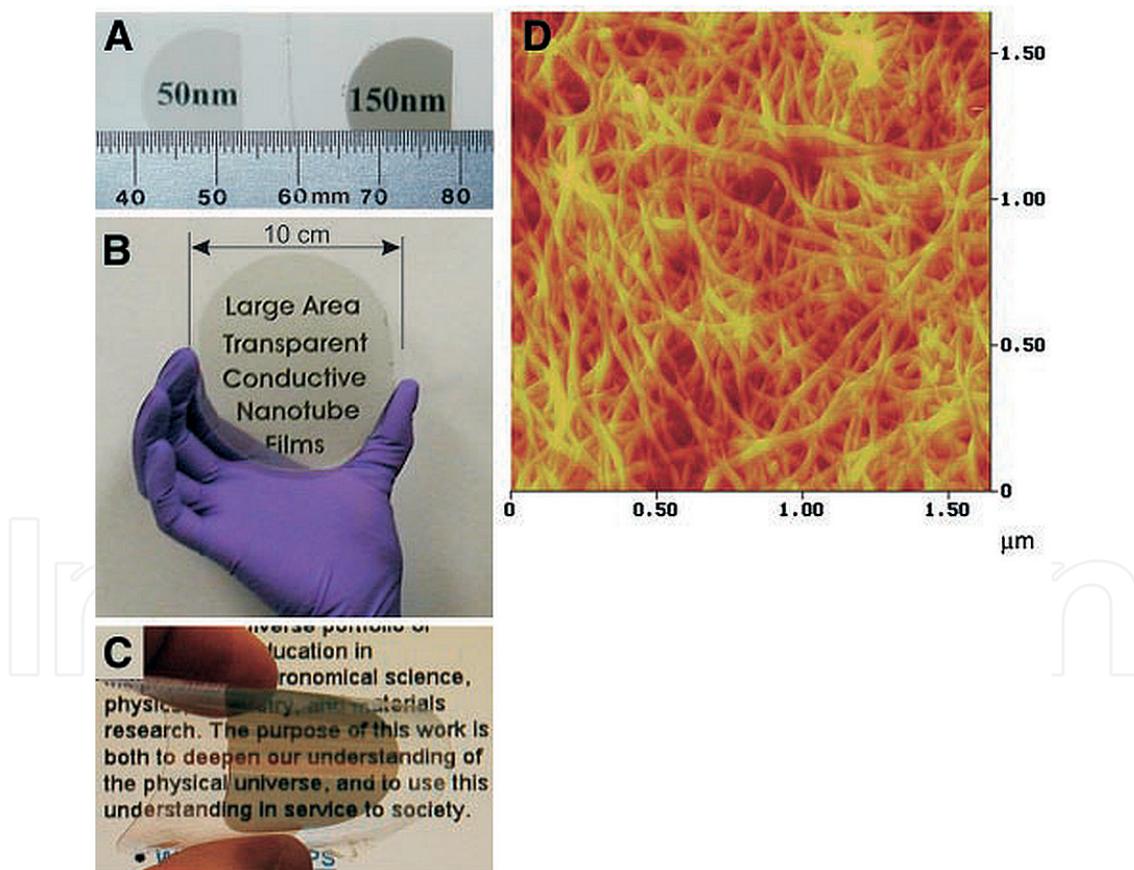


Figure 2. Transparent SWCNT films from A. G. Rinzler's group, taken from reference [33]. (a) Films of the indicated thickness on quartz substrates. (b) A large, 80-nm-thick film on a sapphire substrate 10 cm in diameter. (c) Flexed film on a Mylar sheet. (d) AFM image of a 150-nm-thick t-SWNT film surface (color scale: black to bright yellow, 30 nm). The text in (a)–(c) lies behind the films. From Ref. [33]. Reprinted with permission from AAAS.

Alternatively, as grown SWCNTs (mixed between metallic and semiconducting) can be used and subjected to post-growth separation based on electronic type, that is, metallic or semiconducting. Post-growth separation of SWCNT demonstrated includes dielectrophoresis [26, 27], gel electrophoresis [28], gel agarose chromatography [29, 30], density gradient ultracentrifugation [31], and among others. By enriching the SWCNT population with metallic tubes, the overall conductivity of the fabricated conducting thin films can be increased.

MWCNTs can also be applied to form thin transparent conducting films. Since MWCNTs exhibit metallic behavior, they can be directly processed without further post-growth separation, except for the standard purification step to remove impurities. However, it should be noted that only the outmost shell of the MWCNTs is involved in charge carrier conduction [32].

Because the fabricated CNT films can have a thickness between only a few nanometers up to the order of 100 nanometers, the transmittance can be as high as 95% in the 2–5 μm spectral band [33], which can rival the industry standard indium tin oxide (ITO) films. **Figure 2** shows some example SWCNT transparent thin films produced by vacuum filtration method demonstrated by Wu *et al.* of Zingler's group. The atomic force microscopy analysis (AFM) in **Figure 2D** shows individual SWCNTs randomly intercalated in a network to form an electrically conducting film.

3. Fabrication methods of CNT transparent conducting films

The techniques for forming continuous intercalating network of CNTs to form transparent films can be divided into two main approaches, which is dry processed and solution processed. Solution-processed approach involves dispersing CNTs into solutions, either H_2O based or solvent based. Dispersed CNTs in solution can then be directly deposited on a surface to form a thin film followed by a drying process. The deposition or film forming process can be done by a number of methods including vacuum filtration, dip coating, spin coating, spray coating, direct ink printing, Langmuir-Blodgett technique, and roll-to-roll, among others. Dry-processed approach, as the name suggests, does not involve any use of solution as dispersant for CNTs. The CNTs are either grown directly into a continuous film form or handled directly into films after the CNT synthesis step. In this chapter, both the dry-processed approach and solution-processed approach are discussed briefly.

3.1. Dry-processed approach

The dry-processed approach in producing transparent conducting CNT films that is discussed here involved two methods: pulling of vertically grown MWCNTs and direct film growth on quartz substrate.

In the first method, vertical MWCNT forests grown via catalytic CVD are pulled by hand from a sidewall using an adhesive strip, which was demonstrated by Zhang *et al.* [34]. The pulled MWCNTs from the sidewall will form bundles, which in turn will trap the MWCNTs in the row adjacent to it and pulling them out too, forming a continuous sheet of MWCNTs.

Depending on the size of the supporting substrate of the MWCNT forest, the dimension of a single continuous sheet in a single pull is ~ 5 cm wide and 100 cm long. The fastest pulling rate at which the MWCNTs can self-support itself without breaking is ~ 700 cm/min. However, the pulling technique only work with certain vertically grown MWCNT forest and the allowable pulling rate depends on the forest structure. The resulting sheets of MWCNT appear to be oriented parallel to the pulling direction. From a ~ 245 - μm -high forest, the resulting sheet thickness is ~ 18 μm with an areal density of ~ 2.7 $\mu\text{g}/\text{cm}^2$, and a volumetric density of ~ 0.0015 g/cm^3 [34]. This indicates that in fact, the MWCNT sheets produced are electronically conducting and highly aligned aerogel. The thickness of the sheets can be reduced to ~ 50 nm, effectively increasing the tube density to ~ 0.5 g/cm^3 , by laying them flat on a substrate and immersing it in a liquid where the surface tension will compress the aerogel into thin transparent conducting films. The resulting sheet resistivity was shown to be ~ 700 Ω/\square and transmittance of more than 85% [34].

In the second method, arrays of CNTs are grown parallel to the substrate plane, forming a thin continuous conducting film. It was shown that aligned SWCNTs are grown on monocrystalline ST-cut quartz substrate by using ethanol as the carbon feedstock and Cu as the catalyst [35]. By using this growth method, the SWCNTs will align themselves along the X direction of the ST-cut mono-crystalline quartz surface, similar to the $\langle 100 \rangle$ plane direction in Si wafer. Depending on the density of the catalyst particles, growth of up to 50 SWCNTs per μm can be achieved, with tube length of up to a few millimeters [35]. It is also possible to apply the same growth method to selectively grown semiconducting SWCNTs. This can be done by selectively etching random growing SWCNTs and mixing water vapor with the carbon feedstock to selectively grown SWCNTs of a particular electronic type, in this case semiconducting [25]. Selective growth of metallic SWCNTs should be possible using the same principle by optimizing the correct water vapor to carbon feedstock ratio, or by using a different carbon feedstock. However, it was also shown that aligned SWCNTs do not make high performance transparent conducting film, and that randomly oriented network of SWCNTs is preferred [36]. By using ferritin as the catalyst precursor instead, SWCNTs grown on quartz substrate were parallel to the surface plane but highly random in growth direction. Higher density of SWCNTs can be obtained with resulting sheet resistance of ~ 7.1 $\text{k}\Omega/\square$ and transmittance of up to $\sim 98.4\%$. **Figure 3** shows the scanning electron microscope (SEM) images of randomly oriented (**Figure 3a**) thin film of SWCNTs and aligned array of SWCNTs (**Figure 3b**) grown on the quartz substrate. It is also possible to directly grow CNT-graphene hybrid materials to form transparent conducting films with a sheet resistance of ~ 450 Ω/\square and with transmittance of up to 86% at 550 nm [37].

3.2. Solution-processed approach

Solution-processed approach involved dispersing CNTs into either an aqueous-based solutions or solvents, followed by the deposition process, which can be done through several techniques. The purpose of this dispersion step is to separate CNTs from bundles into isolated suspension of nanomaterials in a solution for easy manipulation and deposition into thin films with controllable parameters. It is known that CNTs tend to bundle up or aggregate together

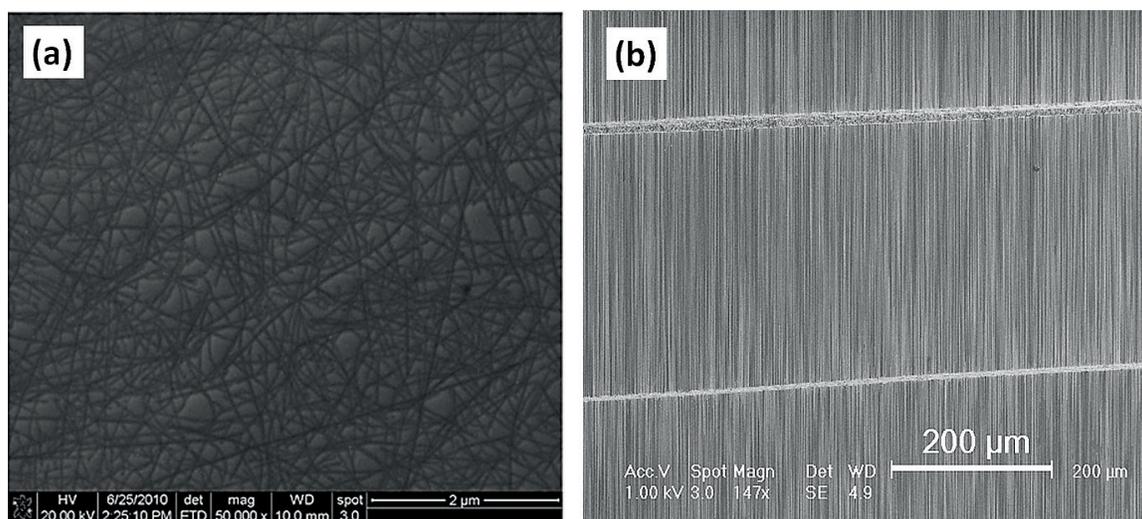


Figure 3. Scanning electron microscopy of SWCNTs directly grown into thin films on quartz substrate. (a) Randomly oriented SWCNTs adapted from Ref. [36], with permission from Elsevier. (b) Aligned array of SWCNTs adapted with permission from Ref. [35]. Copyright (2008) American Chemical Society.

due to the intrinsic electrostatics, especially when they are immersed in a solution. Therefore, to improve the dispersion or “solubility” of CNTs in solutions, particular choice of solution with added surfactants or organic solvents can be used.

There are three main solution types that can be used as dispersant solution: (a) organic solvents or superacids [38], (b) aqueous solution with added dispersing agent or surfactants, and (c) adding functional groups to the CNTs outer wall to counter the intermolecular attraction.

For organic solvents, commonly used solvents are dimethylformamide (DMF), N-methyl-2-pyrrolidone (NMP), toluene, chloroform, dichlorobenzene, and ethylene dichloride (EDC). However, the disadvantages of using organic solvents include low dispersion density of ~ 0.1 mg/mL, very high or very low boiling points of the solvents, and the tendency for the solvents to dissolve other materials involved in the deposition process such as plastics and polymers. Furthermore, depending on the organic solvent use, the dispersed CNTs tend to rebundle or aggregate again if left suspended for a certain period of time.

CNTs can also be dispersed in an aqueous solution mixed with surfactants that acts as surface active agents, which can assist in the dispersion of hydrophobic CNTs due to their amphiphilic properties [39]. Commonly used surfactants are sodium cholate (SC), sodium dodecyl sulfate (SDS), sodium deoxycholate (DOC), and sodium dodecylbenzenesulfonates (SDBS), among others. Nonionic detergent-based surfactants can also be used such as Triton X-100 (Sigma-Aldrich) and Tween 20 (Sigma-Aldrich). Other nonsurfactant solubilization agents that can be used include DNA, cellulose derivatives, porphyrins, starches, polysaccharides, and polymers. The effectiveness of the solubilizing agents and surfactants vary and depends on their head-group charge, inclusion of aromatic ring such as benzene, and also hydrophobic tail.

Another dispersion technique available is functionalization of the exposed CNT carbon atoms with other molecules via covalent bonding to promote affinity between the CNTs and the solution used. Functionalization also negates or reduces the effect of CNTs’ electrostatic attraction between them [40]. Most functionalization materials used are acid based. Although the

resulting dispersion of CNTs will have significantly higher tube concentrations compared to the other two approaches, the conductivity of the produced films may suffer from electrical degradation due to the process induced defects to the CNT sp² structure.

All the dispersion techniques described here require assistance in the form of physical agitation. High power agitation tools such as ultrasonic bath, homogenizer, and physical tip ultrasonic probe may have to be used during the dispersion process. For example, dispersing CNTs in organic solvents requires constant agitation either via ultrasonic bath or ultrasonic tip probe to exfoliate individual CNT from the bundles. Similar technique is also required for CNT in aqueous-based solution with surfactants. Furthermore, this physical agitation also helps to break down impurity particles such as amorphous carbon and catalysts, which can be removed by ultracentrifugation. The heavier catalyst and amorphous carbon particles will be forced to precipitate, while the CNTs remain suspended in the solution as a direct effect of dispersion.

3.3. Film deposition methods

As described earlier, based on the solution-processed approach, there are a few film deposition techniques or methods that can be employed. Here, we will discuss the most commonly used methods, that is, dip coating, spraying, spin coating, vacuum filtration, ink-jet printing, and Langmuir-Blodgett techniques.

3.3.1. Dip coating technique

Dip coating method involves immersing a substrate vertically into a solution with dispersed CNTs and retracting it slowly [2]. Normally, the retracting speed is controlled (typically between 1 and 10 mm/min) to promote CNT adhesion to the substrate layer as the solution near the meniscus evaporates as denoted in **Figure 4**. The dip coating cycle is normally repeated several times to obtain reasonably homogenous and continuous transparent film of several nanometers thick. The thickness of the film can be increased by increasing the number of dip coating cycle to up to 400 times [41]. However, there is a limit to the thickness of the resulting CNT film as it reaches saturation, whereby any additional dip coating cycle will not

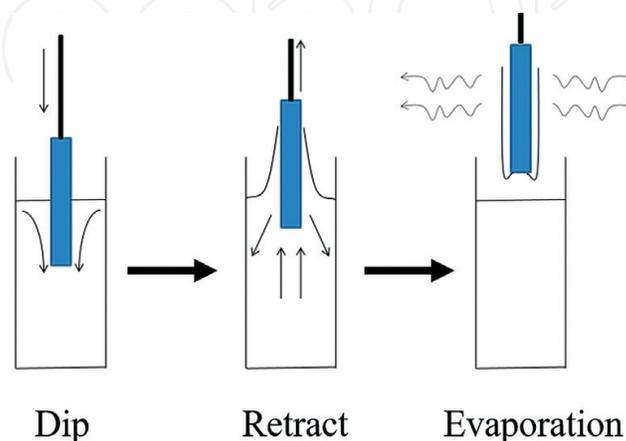


Figure 4. Dip coating technique. Adapted from Ref. [48] with permission from Sains Malaysiana, Universiti Kebangsaan Malaysia.

increase the thickness. For a typical CNT dispersed in organic solvent or aqueous solution with surfactant, maximum film thickness is between 50 and 100 nm, depending on the dispersion concentration and type of CNTs. The typical sheet resistance of a dip-coated CNT film was shown to be $\sim 300 \Omega/\square$ and transmittance of $\sim 85\%$ [41].

3.3.2. *Spraying deposition technique*

The spraying deposition technique involves blowing compressed air through the droplets of CNT dispersion. Typically used tool is the artist air-brush, which has been shown to produce thin, uniform film of CNTs on the substrate surface [41, 42]. The CNTs used are dispersed in aqueous solution with added surfactants such as SDS or SDBS. In this technique, water in the aqueous solution will dry up almost immediately as the spray droplets touch the substrate during spraying. This negates the effect of water droplet surface tension pulling CNTs to clump together during drying as in the dip-coating or spin-coating methods, dubbed as the coffee ring effect. It is also important to control the spraying parameters to make sure that the solution in the CNT dispersion dries on contact and not before. Premature drying will lead to dry CNTs that do not form good electrical contacts within the film network. However, it is difficult to control the drying of the solution and to estimate when complete drying has been achieved. It was shown that at film thickness of ~ 26 nm, the resulting sheet resistance was measured to be $\sim 57 \Omega/\square$ (conductivity, $\sigma \sim 6704$ S/cm) and transmittance of $\sim 65\%$. Although, spray deposited CNT film shows high conductivity, the transmittance is relatively lower. It was also shown that comparing CNT films with sheet resistance of $\sim 475 \Omega/\square$ deposited via dip coating and spray coating, the transmittance is ~ 83 and $\sim 73\%$, respectively [41].

3.3.3. *Spin-coating technique*

The spin-coating technique employs similar tools for photolithography. A spin coater is used to spin a substrate after a deposition of CNT dispersion for even distribution [1]. This technique relies on the CNTs to form physisorption or adhesion to the substrate surface as the solution is pushed out due to the centripetal force. It may be essential to first coat the substrate with silane-based self-assembled monolayer (ASM) to promote adhesion between the CNT and the substrate surface. The spin cycle has to be repeated several times until a continuous homogeneous CNT film is obtained. This method is simple but uses a lot of materials because most of the CNTs deposited during spinning will be washed out along with the solution. Consequently, this method is more suitable to be used with CNTs that are dispersed in organic solvents with low boiling points such as EDC and chloroform, where the solvents will dry up quickly during spinning and promote adhesion between the CNT and the substrate. The resulting CNT film will exhibit varying characteristics. One study has shown that by using CNT in EDC for spin coating, a film thickness of 24 nm was produced with a sheet resistance of $\sim 128 \Omega/\square$ ($\sigma \sim 4629$ S/cm) and transmittance at 550 nm of $\sim 90\%$.

3.3.4. *Vacuum filtration technique*

The vacuum filtration technique is straight forward and easy, as described in the detail in [33, 38]. Purified dispersion of CNTs in aqueous solution with surfactant or in superacids is first obtained as previously described. Here, any surfactant can be used. Basically, a diluted CNT dispersed in

solution is filtered through a membrane filter using a vacuum filtration apparatus. The filtered CNT on the membrane will form a continuous thin film of CNT. It is recommended to use mixed cellulose ester (MCE) membrane filter with $\sim 0.2 \mu\text{m}$ pore size [33]. Effectively, the size of the CNT film produced is limited by the vacuum filtration apparatus size or the filtering membrane size.

The following are essential steps to follow in order to obtain good transparent CNT film. The vacuum filtration apparatus is first equipped with the suitable membrane filter and is turned on. Solution of dispersed CNT is slowly and carefully pipetted into the filter reservoir funnel, while preventing the formation of bubbles. Any agitation due to fast water flow movements or bubbles will affect the continuity and homogeneity of the resulting CNT film. Additional CNT in solution can be added to achieve desired film thickness. After all the solutions have been filtered, the vacuum pump is left on for ~ 20 minutes to aid drying of the membrane filter. Deionized water is then pipetted inside the filter reservoir to wash out any residual surfactants until none is visible. After further drying, the CNT film on the membrane filter is then ready to be transferred onto a substrate.

To transfer the CNT film onto another substrate, it must be first removed from the filter membrane. The CNT film cannot be peeled off of the membrane filter due to the strong adhesion between the CNT and the membrane. Therefore, the membrane must be removed by dissolving it in organic solvents such as acetone. The membrane can be carefully immersed in an acetone bath until all visible traces of MCE membrane is gone. The floating CNT film can then be picked up using the substrate or using a sieve before transferring it onto a substrate. It is also possible to use poly(ethylene terephthalate) (PET) as the substrate. Subsequent washing of the film on substrate with acetone or other suitable solvent is repeated to remove the remaining traces of membrane filter. Annealing of the substrate at $\sim 90^\circ\text{C}$ can help improve adhesion between the CNT film and the substrate. It is possible to use flexible transparent material as the substrate, as depicted in **Figure 2**, which is the example of films produced via vacuum filtration method. **Figure 5a** shows CNT filtered on a membrane, and **Figure 5b** shows the CNT transparent film on glass substrate after membrane removal and film transfer.

Transparent CNT films produced by vacuum filtration method show promising conductivity to transmittance performance. Results showed an average conductivity, σ , of $\sim 2000 \text{ S/cm}$ with corresponding transmittance of $\sim 93\%$ at 550 nm wavelength [38]. Others have reported films of 50-nm thick to exhibit $>90\%$ transmittance and sheet resistance of $30 \Omega/\square$ [33].

Vacuum filtration method is very attractive due to several advantages such as first, high homogeneity of the film. Second, the force created by the vacuum pump helps the orientation of CNTs to be parallel to the surface, and therefore improves CNT to CNT electrical contacts. Last, the film thickness can be controlled by either varying the CNT solution concentration or varying the amount of solution that are filtered.

3.3.5. Ink-jet printing technique

CNT “inks” can be used to print thin CNT films on transparent substrate by using conventional bubble jet printers. One example of CNT ink is by mixing CNTs with water-soluble conducting polymer and poly(2-methoxyaniline-5-sulfonic acid) (PMAS) as shown by [43]. A

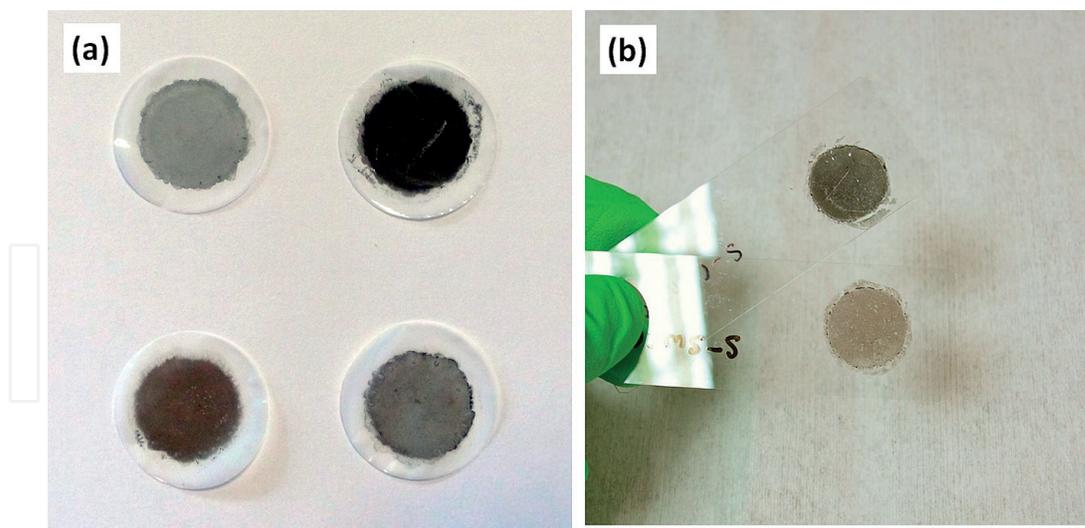


Figure 5. CNT films produced via vacuum filtration. (a) Membrane filters with CNT film of various thicknesses. (b) CNT transparent film after membrane removal and transfer on glass substrate.

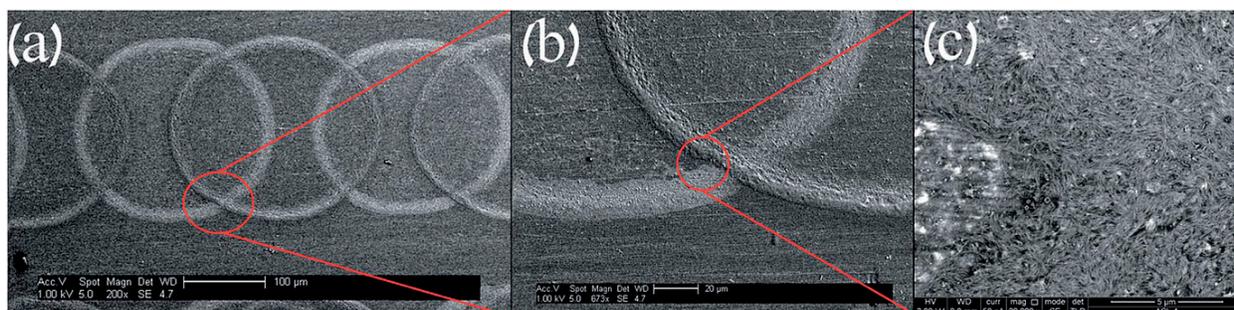


Figure 6. SEM images of connected ink-jet CNT droplet rings. Adapted from Ref. [44] with permission of The Royal Society of Chemistry.

single printed layer of CNT ink demonstrates a sheet resistance of $\sim 100 \text{ k}\Omega/\square$ (conductivity, σ , $\sim 0.93 \text{ S/cm}$) with transmittance of $\sim 85\%$. Interestingly, increasing the number of printed layers to four resulted in the reduction of sheet resistance by approximately a factor of two, but decreases the transmittance by no more than 10% [43].

It was also discovered that the ink-jet droplets can exhibit surface tension that can aggregate CNTs into bundles in the so-called coffee ring effect [44]. The surface tension of the ink-jet droplets created a uniform ring of CNT as thick as 300 nm that aggregate together as shown in **Figure 6**. By connecting each droplet ring to each other, a conducting network layer of CNT film has been produced by [44]. After temperature treatment, the resulting film exhibit sheet resistance as low as $1000 \Omega/\square$, while the transmittance was $\sim 75\%$. The printed pattern of the network of CNT ring droplets can be adjusted to optimize the transparent conductor's performance.

3.3.6. Langmuir-Blodgett technique

Langmuir-Blodgett (LB) technique involves the self arrangement of organic material, including nanoparticles, forming a monolayer on the surface of a liquid in a trough. An LB film of

CNTs will be formed when there is an interaction at the water-air interface, whereby the naturally hydrophilic CNTs tend to aggregate at the surface. If the CNT concentration is less than the critical micellar concentration (CMC), the CNTs will arrange themselves as a monolayer film parallel to the liquid surface. The density of the CNT LB film can be increased by pushing the liquid surface with a pedal-like instrument toward the center of the trough. Once a dense and aligned monolayer of CNT LB film is formed, a substrate can be immersed in the trough either parallel or perpendicular to the liquid surface where the film will then be absorbed onto the substrate's surface. The substrate immersion step is similar to the dip coating technique.

The CNT use in LB technique is usually dispersed and sonicated in organic compound with low boiling point and lower density than water such as chloroform. CNT dispersed in chloroform is then carefully released on the surface of the liquid (typically deionized water) in the trough forming a monolayer of CNTs. Care must be taken to ensure that the density of CNT is less than the CMC. When the chloroform completely evaporates, the CNT LB film will remain suspended on the liquid surface ready to be compressed and transferred on a transparent substrate. To increase adhesion of the CNT LB film on the substrate, surface treatment with a primer or silane-based SAM.

A single layer of SWCNT LB film can have a thickness ~ 3 nm, which is slightly higher than a typical SWCNT monolayer thickness due to the formation of bundles [45]. The LB process can be repeated to obtain thicker films. Since each LB process produces approximately monolayer CNT film, it possible to control the film thickness in the order of ~ 3 nm. A SWCNT LB film of ~ 300 nm thickness has been demonstrated by repeating the process 99 times [45]. In contrast, the dip coating technique does not offer tight control of CNT layer thickness after each subsequent dipping, and there is a limit to the maximum thickness that can be obtained depending on the adhesion or absorption sites that are available on the substrate's surface.

It is reported that a SWCNT LB film of ~ 120 nm thick showed a transmittance of around 80–90% across the visible light spectrum [45]. This figure is comparable to the transmittance that of 20-nm thick film fabricated via the vacuum filtration method. **Figure 7** shows

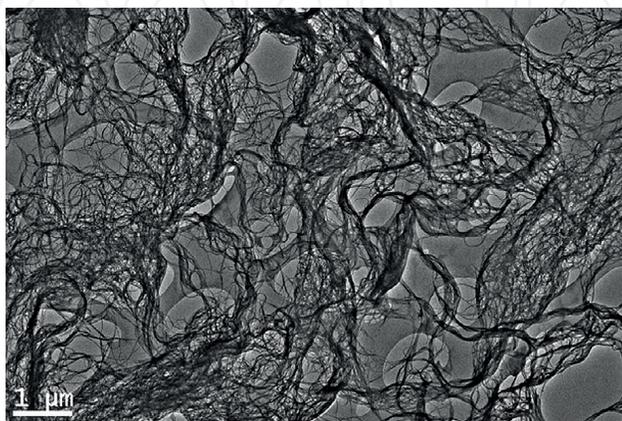


Figure 7. Transmission electron micrograph image of a 3-layer SWCNT LB film on an amorphous carbon grid. Adapted from Ref. [45] with permission from Elsevier.

a transmission electron microscope (TEM) image of a SWCNT LB film on carbon grid. The conductivity of the transparent film produced via the LB technique is dependent on the substrate orientation during the dipping step. Parallel direction of dipping showed the highest conductivity, followed by 45° angled and perpendicular directions, which showed the lowest value.

Although it is relatively easy to control the film thickness in the LB method, the electrical performance is generally inferior compared to other methods such as vacuum filtration and dip coating due to the poor intermolecular contact between adjacent CNTs in the film. This intermolecular contact can be improved by employing the hybrid film structure consisting of graphene oxide and SWCNTs via the LB method [46, 47]. This hybrid LB film exhibits the highest sheet resistance of 50,000 Ω/\square at a transmittance of $\sim 97\%$ and the lowest sheet resistance of 200 Ω/\square at 77% transmittance.

4. Comparison of transparent film performance

Generally, there exist a trade-off of CNT-based transparent conductor between the optical performance and the electrical performance. CNT transparent film with high transmittance exhibits reduced conductivity (or higher sheet resistance) and vice versa. However, there is another factor that affects the electrical performance of the film, which is the fabrication method or the film deposition method used. The inconsistency between the performances of the films produced by different methods may be due to the different intermolecular contact between adjacent CNTs in the film network. Discrepancy in the tube-tube contact resistance can result in significant collective conductivity of the whole film.

To study or quantify the tube-tube intermolecular contact resistances in CNT films from each fabrication method is difficult. One study has shown that in a controlled experiment, CNT transparent film fabrication via vacuum filtration method shows the best electrical conductivity, followed by dip coating and LB [48]. On the other hand, in terms of the transmittance, LB films show the highest transmittance, followed by dip coating and vacuum filtration. It is projected that a CNT transparent film fabricated via vacuum filtration with the same transmittance value with an LB film will show superior electrical conductivity due to the reduced intermolecular contact resistance between adjacent CNTs.

5. Conclusion

In this chapter, the basic theoretical background of carbon nanotube and its application as transparent film conductor have been discussed. The film fabrication methods available have also been discussed, along with the inherent advantages and disadvantages of each method. CNT-based transparent conductors have shown optical and electrical performance that rival that of ITO. Furthermore, CNT-based films can be applied on flexible substrates

and do not suffer from temperature induced structural degradation as in other polymer- or organic-based films.

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Conflict of interest

The author declares no conflict of interest.

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References

- [1] Farbod M, Zilaie A, Kazeminezhad I. Carbon nanotubes length optimization for preparation of improved transparent and conducting thin film substrates. *Journal of Science-Advanced Materials and Devices*. 2017;**2**(1):99-104
- [2] He Y, Jin H, Qiu S, Li Q. A novel strategy for high-performance transparent conductive films based on double-walled carbon nanotubes. *Chemical Communications*. 2017;**53**(20): 2934-2937
- [3] Tsapenko AP, Goldt AE, Shulga E, Popov ZI, Maslakov KI, Anisimov AS, et al. Highly conductive and transparent films of H₂AuCl₄-doped single-walled carbon nanotubes for flexible applications. *Carbon*. 2018;**130**:448-457

- [4] Yu Y, Luo Y, Guo A, Yan L, Wu Y, Jiang K, et al. Flexible and transparent strain sensors based on super-aligned carbon nanotube films. *Nanoscale*. 2017;**9**(20):6716-6723
- [5] Jeon I, Yoon J, Ahn N, Atwa M, Delacou C, Anisimov A, et al. Carbon nanotubes versus graphene as flexible transparent electrodes in inverted perovskite solar cells. *Journal of Physical Chemistry Letters*. 2017;**8**(21):5395-5401
- [6] Pyo S, Kim W, Jung H, Choi J, Kim J. Heterogeneous Integration of Carbon-Nanotube-Graphene for High-Performance, Flexible, and Transparent Photodetectors. *Small*. 2017;**13**(27)
- [7] Wildoer JWG, Venema LC, Rinzler AG, Smalley RE, Dekker C. Electronic structure of atomically resolved carbon nanotubes. *Nature*. 1998;**391**(6662):59-62
- [8] Thess A, Lee R, Nikolaev P, Dai H, Petit P, Robert J, et al. Crystalline ropes of metallic carbon nanotubes. *Science*. 1996;**273**(5274):483-487
- [9] Avouris P. Carbon nanotube electronics. *Chemical Physics*. 2002;**281**(2-3):429-445
- [10] White C, Todorov T. Carbon nanotubes as long ballistic conductors. *Nature*. 1998;**393**(6682):240-242
- [11] Hone J, Whitney M, Zettl A. Thermal conductivity of single-walled carbon nanotubes. *Synthetic Metals*. 1999;**103**(1-3):2498-2499
- [12] Wong EW, Sheehan PE, Lieber CM. Nanobeam mechanics: Elasticity, strength, and toughness of nanorods and nanotubes. *Science*. 1997;**277**(5334):1971-1975
- [13] Yu MF, Lourie O, Dyer MJ, Moloni K, Kelly TF, Ruoff RS. Strength and breaking mechanism of multi-walled carbon nanotubes under tensile load. *Science*. 2000;**287**(5453):637-640
- [14] Schonenberger C, Bachtold A, Strunk C, Salvetat JP, Forro L. Interference and Interaction in multi-wall carbon nanotubes. *Applied Physics A: Materials Science and Processing*. 1999;**69**(3):283-295
- [15] de Heer WA, Martel R. Industry sizes up nanotubes. *Physics World*. 2000;**13**(6):49-53
- [16] Ebbesen TW, Ajayan PM. Large-scale synthesis of carbon nanotubes. *Nature*. 1992;**358**(6383):220-222
- [17] Dai HJ, Kong J, Zhou CW, Franklin N, Tomblor T, Cassell A, et al. Controlled chemical routes to nanotube architectures, physics, and devices. *The Journal of Physical Chemistry. B*. 1999;**103**(51):11246-11255
- [18] Baker RTK. CATALYTIC GROWTH OF CARBON FILAMENTS. *Carbon*. 1989;**27**(3):315-323
- [19] Li YM, Mann D, Rolandi M, Kim W, Ural A, Hung S, et al. Preferential growth of semiconducting single-walled carbon nanotubes by a plasma enhanced CVD method. *Nano Letters*. 2004;**4**(2):317-321
- [20] Nikolaev P, Bronikowski MJ, Bradley RK, Rohmund F, Colbert DT, Smith KA, et al. Gas-phase catalytic growth of single-walled carbon nanotubes from carbon monoxide. *Chemical Physics Letters*. 1999;**313**(1-2):91-97

- [21] Kitiyanan B, Alvarez WE, Harwell JH, Resasco DE. Controlled production of single-wall carbon nanotubes by catalytic decomposition of CO on bimetallic Co-Mo catalysts. *Chemical Physics Letters*. 2000;**317**(3-5):497-503
- [22] Maruyama S, Kojima R, Miyauchi Y, Chiashi S, Kohno M. Low-temperature synthesis of high-purity single-walled carbon nanotubes from alcohol. *Chemical Physics Letters*. 2002;**360**(3-4):229-234
- [23] Hecht D, Hu L, Irvin G. Emerging transparent electrodes based on thin films of carbon nanotubes, graphene, and metallic nanostructures. *Advanced Materials*. 2011;**23**(13):1482-1513
- [24] Zhao M-Q, Tian G-L, Zhang Q, Huang J-Q, Nie J-Q, Wei F. Preferential growth of short aligned, metallic-rich single-walled carbon nanotubes from perpendicular layered double hydroxide film. *Nanoscale*. 2012;**4**(7):2470-2477
- [25] Li J, Liu K, Liang S, Zhou W, Pierce M, Wang F, et al. Growth of high-density-aligned and semiconducting-enriched single-walled carbon nanotubes: Decoupling the conflict between density and selectivity. *ACS Nano*. 2014;**8**(1):554-562
- [26] Krupke R, Hennrich F, von Lohneysen H, Kappes MM. Separation of metallic from semiconducting single-walled carbon nanotubes. *Science*. 2003;**301**(5631):344-347
- [27] Mattsson M, Gromov A, Dittmer S, Eriksson E, Nerushev OA, Campbell EEB. Dielectrophoresis-induced separation of metallic and semiconducting single-wall carbon nanotubes in a continuous flow microfluidic system. *Journal of Nanoscience and Nanotechnology*. 2007;**7**(10):3431-3435
- [28] Tanaka T, Jin HH, Miyata Y, Kataura H. High-yield separation of metallic and semiconducting single-wall carbon nanotubes by agarose gel electrophoresis. *Applied Physics Express*. 2008;**1**(11)
- [29] Liu H, Nishide D, Tanaka T, Kataura H. Large-scale single-chirality separation of single-wall carbon nanotubes by simple gel chromatography. *Nature Communications*. 2011;**2**:309
- [30] Yahya I, Bonaccorso F, Clowes SK, Ferrari AC, Silva SRP. Temperature dependent separation of metallic and semiconducting carbon nanotubes using gel agarose chromatography. *Carbon*. 2015;**93**:574-594
- [31] Arnold MS, Green AA, Hulvat JF, Stupp SI, Hersam MC. Sorting carbon nanotubes by electronic structure using density differentiation. *Nature Nanotechnology*. 2006;**1**(1):60-65
- [32] Collins PG, Hersam M, Arnold M, Martel R, Avouris P. Current saturation and electrical breakdown in multi-walled carbon nanotubes. *Physical Review Letters*. 2001;**86**(14):3128-3131
- [33] Wu ZC, Chen ZH, Du X, Logan JM, Sippel J, Nikolou M, et al. Transparent, conductive carbon nanotube films. *Science*. 2004;**305**(5688):1273-1276

- [34] Zhang M, Fang SL, Zakhidov AA, Lee SB, Aliev AE, Williams CD, et al. Strong, transparent, multifunctional, carbon nanotube sheets. *Science*. 2005;**309**(5738):1215-1219
- [35] Ding L, Yuan DN, Liu J. Growth of high-density parallel arrays of long single-walled carbon nanotubes on quartz substrates. *Journal of the American Chemical Society*. 2008; **130**(16):5428
- [36] Shi D, Resasco DE. Study of the growth of conductive single-wall carbon nanotube films with ultra-high transparency. *Chemical Physics Letters*. 2011;**511**(4-6):356-362
- [37] Duc Dung N, Tai N-H, Chen S-Y, Chueh Y-L. Controlled growth of carbon nanotube-graphene hybrid materials for flexible and transparent conductors and electron field emitters. *Nanoscale*. 2012;**4**(2):632-638
- [38] Hecht DS, Heintz AM, Lee R, Hu L, Moore B, Cucksey C, et al. High conductivity transparent carbon nanotube films deposited from superacid. *Nanotechnology*. 2011;**22**(7)
- [39] Rastogi R, Kaushal R, Tripathi SK, Sharma AL, Kaur I, Bharadwaj LM. Comparative study of carbon nanotube dispersion using surfactants. *Journal of Colloid and Interface Science*. 2008;**328**(2):421-428
- [40] Huang WJ, Lin Y, Taylor S, Gaillard J, Rao AM, Sun YP. Sonication-assisted functionalization and solubilization of carbon nanotubes. *Nano Letters*. 2002;**2**(3):231-234
- [41] Song YI, Yang C-M, Kim DY, Kanoh H, Kaneko K. Flexible transparent conducting single-wall carbon nanotube film with network bridging method. *Journal of Colloid and Interface Science*. 2008;**318**(2):365-371
- [42] Kim S, Yim J, Wang X, Bradley DDC, Lee S, de Mello JC. Spin- and spray-deposited single-walled carbon-nanotube electrodes for organic solar cells. *Advanced Functional Materials*. 2010;**20**(14):2310-2316
- [43] Small WR, Panhuis MIH. Inkjet printing of transparent, electrically conducting single-walled carbon-nanotube composites. *Small*. 2007;**3**(9):1500-1503
- [44] Shimoni A, Azoubel S, Magdassi S. Inkjet printing of flexible high-performance carbon nanotube transparent conductive films by "coffee ring effect". *Nanoscale*. 2014;**6**(19):11084-11089
- [45] Massey MK, Pearson C, Zeze DA, Mendis BG, Petty MC. The electrical and optical properties of oriented Langmuir-Blodgett films of single-walled carbon nanotubes. *Carbon*. 2011; **49**(7):2424-2430
- [46] Zheng Q, Zhang B, Lin X, Shen X, Yousefi N, Huang Z-D, et al. Highly transparent and conducting ultralarge graphene oxide/single-walled carbon nanotube hybrid films produced by Langmuir-Blodgett assembly. *Journal of Materials Chemistry*. 2012;**22**(48):25072-25082

- [47] Yang T, Yang J, Shi L, Maeder E, Zheng Q. Highly flexible transparent conductive graphene/single-walled carbon nanotube nanocomposite films produced by Langmuir-Blodgett assembly. *RSC Advances*. 2015;5(30):23650-23657
- [48] Yahya I, Theng L, Mustaza S, Abdullah H, Amin N. Characterization of transparent conducting carbon nanotube thin films prepared via different methods. *Sains Malaysiana*. 2017;46(7):1103-1109

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