Physics and applications of aligned carbon nanotubes

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Physics and applications of aligned carbon nanotubes

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Ever since the discovery of carbon nanotubes (CNTs) by Iijima in 1991, there have been extensive research efforts on their synthesis, physics, electronics, chemistry, and applications due to the fact that CNTs were predicted to have extraordinary physical, mechanical, chemical, optical, and electronic properties. Among the various forms of CNTs, single-walled and multi-walled, random and aligned, semiconducting and metallic, aligned CNTs are especially important since fundamental physics studies and many important applications will not be possible without alignment. Even though there have been significant endeavors on growing CNTs in an aligned configuration since their discovery, little success had been realized before our first report on growing individually aligned CNTs on various substrates by plasma-enhanced chemical vapor deposition (PECVD) [Science 282 (1998) 1105-1108]. Our report spearheaded a new field on growth, characterization, physics, and applications of aligned CNTs. Up to now, there have been thousands of scientific publications on synthesizing, studying, and utilizing aligned CNTs in various aspects. In this communication, we review the current status of aligned CNTs, the physics for their alignment, their applications in field emission, optical antennas, subwavelength light transmission in CNT-based nanocoax structures, nanocoax arrays for novel solar cell structures, etc.

The focus of this review is to examine various aligned CNT systems, either as an individual or as an array, either the orientation is vertical, parallel, or at other angles to the substrate horizon, either the CNT core structures are mostly hollow channels or are composed of complex compartments. Major fabrication methods are illustrated in detail, particularly the most widely used PECVD growth technique on which various device integration schemes are based, followed by applications whereas current limitations and challenges will also be discussed to lay down the foundation for future developments.

PACS: 61.48.De Structure of carbon nanotubes, boron nanotubes, and other related systems, 85.35.Kt Nanotube devices, 81.07.-b Nanoscale materials and structures: fabrication and characterization, 01.30.Rr Surveys and tutorial papers; resource letters

Keywords: carbon nanotubes; aligned arrays

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1. Introduction
Carbon nanotubes (CNTs) and related nanostructures have been one of the most scientifically studied material systems in the recent years ever since their well-known experimental discovery [1]. A large variety of potential applications have been envisioned, some of which have already been reduced to practice, while others are still under study. The most intriguing properties of CNTs lie in their unique quasi-one-dimensional nanoscale structures that are intrinsically anisotropic: properties in the longitudinal direction are drastically different from those in the azimuthal directions. It is critical in most applications to know and control how a CNT is oriented either as a stand-alone individual or in a group of many. And it is obviously more challenging and more desirable to obtain a CNT ensemble with all its members having a common orientation, something usually referred to as an aligned CNT array. Such an array, in many ways, preserves the anisotropic properties of individual CNTs, and in the mean time can be more robust and larger in its physical size as a whole, which greatly facilitates their integration into practical devices. As a necessary introduction, we will first review the fundamental structures of CNTs, their unique anisotropic properties, and the general growth mechanisms by chemical vapor deposition (CVD), without specifying their orientation or alignment. This will carry out the necessary preparation for the following in-depth review of the state-of-the-art discoveries and progresses in the fabrication and applications of aligned CNT arrays.

1.1. Discovery of CNTs
The well-known allotropes of carbon are diamond, graphite, amorphous carbon, and fullerenes discovered in 1985 [2]. Fullerene is entirely composed of carbon in the form of a hollow sphere (buckyball) or ellipsoid. Figure 1 shows the crystallographic structures of the four allotropes of carbon. CNTs (also called buckytubes in earlier days) are elongated cylindrical fullerenes with diameters of subnanometer to tens of nanometers depending on the number of graphitic layers and lengths of submicron to hundreds of or even thousands of microns.

The length of the CNT ranges from less than a micron to several millimeters. The carbon atoms in a CNT are bonded trigonally in a curved sheet (graphitic layer) that forms a hollow cylinder. Such unique nanostructures result in many extraordinary properties such as high tensile strength,
high electrical and thermal conductivities, high ductility, high thermal and chemical stability, which makes them suitable for various applications as discussed in Sections 4 and 5.

CNTs are typically categorized as single-walled (SWCNTs), double-walled (DWCNTs), and multi-walled (MWCNTs) with respect to the number of graphitic layers. The nature of the atomic bonding in a CNT is described by applied quantum chemistry or, specifically, orbital hybridization. The chemical bonds in CNTs are all sp² bonds, similar to those of graphite. The details of atomic structure of individual CNTs are well described in previous reviews.

The CNTs have an arguably long history of discovery. It was speculated [3] that the first carbon filament was possibly synthesized as early back as 1889 [4] at Thomas Alva Edison’s era when a light bulb filament was searched for incandescent lamps. Carbon filaments were then produced by a thermal decomposition of gaseous hydrocarbon (methane) to make light bulb filaments. In that era, carbon filaments smaller than a few microns in diameter could not be observed because of the low resolution of the optical microscopes used at the time. Based on the experimental method and conditions described in the corresponding patent, it is conceivable that hollow carbon filaments were possibly produced then [3], although no images were recorded as direct evidences.

The first transmission electron microscopy (TEM) evidence for the tubular nature of nanoscale carbon filaments was published in 1952 [5]. Clear TEM images of hollow carbon filaments were published, as shown in Figure 2(a), which clearly illustrates that the carbon filaments are hollow tubes with diameters of about 50 nm. The graphitic walls are clearly observed from the TEM image contrast. The structures seem to be multi-walled with 15–20 layers [3]. In 1973, Boehm reported hollow carbon fibers by catalytic disproportionation of carbon monoxide at 480–700°C [7]. In 1976, hollow carbon fibers with nanometer-scale diameters were synthesized using a vapor-growth technique [6]. The reported TEM image (Figure 2(b)) clearly shows that the hollow fiber consists of a single graphitic layer. In 1979, hollow carbon fibers were produced on carbon anodes during arc discharge and presented in a conference [8]. These hollow tubular nanostructures were grown in a nitrogen atmosphere at low pressures. In 1987, a patent to produce “cylindrical discrete carbon fibrils” with a “constant diameter between about 3.5 and about 70 nanometers . . . , length 102 times the diameter, and an outer region of multiple essentially continuous layers of ordered carbon atoms and a distinct inner core . . .” was issued [9]. Some scientists even believed that hollow carbon nanostructures were likely produced in ancient forging (AD 900–1800) although, of course, nobody noticed them at that time [10]. Most of the work before 1991 were unfortunately not well known by the broader scientific community, nor were the hollow carbon structures called “carbon nanotubes”, and therefore not creating a significant impact.

Figure 2. Typical hollow carbon fiber images in the history. (a) First TEM images of possible MWCNTs published in 1952; (b) first TEM image of possible SWCNTs published in 1976. (a) Reprinted from Carbon, 44, M. Monthioux and V.L. Kuznetsov, pp. 1621–1623 [3]. Copyright (2006), with permission from Elsevier. (b) Reprinted from Journal of Crystal Growth, 32, M. Oberlin et al., pp. 335–349 [6]. Copyright (1976), with permission from Elsevier.
Since buckminster fullerene (shown in Figure 1(d)) was discovered by arc discharge in 1985 [2], more and more scientists expressed interests in nanomaterials. Shortly after, Iijima, using the same method (arc discharge) to produce C₆₀, found that the central core of the cathodic deposit contained a variety of closed graphitic structures including nanoparticles and nanotubes [1]. The obtained CNTs were MWCNTs as shown in Figure 3(a). The work was published in *Nature* in 1991 and has been noticed worldwide in the scientific community. It is fair to say that the report of CNTs by Iijima strengthened the scientific community’s pursuit to nanoscience and nanotechnology. Readers interested in the CNT discovery stories are referred to the related literatures [3,13,14], especially the editorial paper written by Monthioux and Kuznetsov in *Carbon* [3].

Following the research of MWCNTs by Iijima in 1991, SWCNTs were independently synthesized using arc-discharge techniques (see Figure 3(b) and (c)) by adding transition-metal catalysts (Fe [11] or Co [12]). The synthesis of SWCNTs is an important milestone in the development of CNT research because many theoretical predications of CNT properties can be more conveniently tested on the simplest SWCNT structures.

The arc-discharge-produced materials are mixtures of amorphous carbon, graphite, and CNTs with a low CNT yield. Pure CNTs are usually obtained by various purification methods [15–20]. Although the yield is low and the purification procedure is complex, the produced CNTs have good crystallinity and very few defects. So the method is still widely used today. In 1995, an alternative method of preparing SWCNTs, laser vaporization of graphite, was discovered by Smalley’s group [21]. This method resulted in a high yield of SWCNTs with unusually uniform diameters [22].

Besides the above classic CNT structures, hybrid CNTs, such as CNT Y-junctions [23–26] (Figure 4(a) and (b)) and CNT nanobuds [27,29] (Figure 4(c)), are also discovered. CNT nanotorus (Figure 4(d)) is also predicted. They are, however, beyond the content of this review.

Along with the synthesis of individual CNTs, CNT arrays consisting of a number of individual CNTs were also fabricated at the same time. CNT ropes consisting of 100–500 aligned SWCNTs in a closely stacked two-dimensional triangular lattice arrangement were reported as early as in 1996 using a laser ablation method (Figure 5) [22]. SWCNT ropes were synthesized from a carbon–nickel–cobalt mixture at 1200°C. These SWCNTs are nearly uniform in diameter and self-organize into “ropes” consisting of 100 to 500 SWCNTs with a SWCNT spacing of 17 Å.

Later, large-scale MWCNTs were fabricated from iron nanoparticles embedded in mesoporous silica by pyrolysis of acetylene using a CVD method (Figure 6) [30]. The MWCNTs grown from

![Figure 3. High-resolution TEM (HRTEM) images of the most well-known (a) MWCNTs published in 1991 [1], (b) SWCNTs published in 1993 grown from iron catalyst [11], and (c) SWCNTs published simultaneously with (b) using another catalyst, cobalt [12]. All these CNTs were synthesized by DC arc-discharge evaporation of carbon. (a) Reprinted by permission from Macmillan Publishers Ltd: Nature [1], copyright (1991). (b) Reprinted by permission from Macmillan Publishers Ltd: Nature [11], copyright (1993). (c) Reprinted by permission from Macmillan Publishers Ltd: Nature [12], copyright (1993).](image-url)
Figure 4. (a) TEM image of CNT Y-junction; (b) SEM image of CNT Y-junction with a smooth surface; (c) TEM image of CNT nanobuds in which a fullerene is combined with an SWCNT and attached to the surface of the SWCNT. Inset is the structure of the nanobud on an SWCNT. (d) A predicted CNT nanotorus. (a) Reprinted by permission from Macmillan Publishers Ltd: Nature [23], copyright (1999). (b) Reprinted with permission from W.Z. Li et al., Applied Physics Letters 79, pp. 1879–1881, 2001 [24]. Copyright (2001), American Institute of Physics. (c) Reprinted by permission from Macmillan Publishers Ltd: Nature Nanotechnology [25], copyright (2007). (d) Reprinted figure with permission from L. Liu et al., Physical Review Letters 88, p. 217206, 2002 [26]. Copyright (2002) by the American Physical Society.

Figure 5. TEM images of an SWCNT rope prepared by laser vaporization of graphite in 1996. (a) A single SWCNT rope made up of ~100 SWCNTs as it bends through the image plane of the microscope, showing uniform diameter and triangular packing of the tubes within the rope. (b) Side view of a rope segment. From A. Thess et al., Science, 273, pp. 483–487, 1996 [22]. Reprinted with permission from AAAS.

the iron nanoparticles embedded in mesoporous silica are approximately perpendicular to the surface of the silica and form an aligned array of isolated tubes with a tube spacing of about 100 nm [30]. It is believed that some catalytic iron nanoparticles were embedded in the vertical cylindrical pores. When CNTs grew in these vertical pores, they became perpendicular to the surface of the silica substrate. Those formed on iron nanoparticles embedded in inclined cylindrical pores were tilted along the axes of the pores. The growth direction of the nanotubes can be controlled by the pores from which the nanotubes grow. These MWCNTs were randomly grown
on the substrates, not very straight, and very often entangled together. Large-scale MWCNTs were also fabricated from thin films of cobalt catalysts patterned on a silica substrate by pyrolysis of 2-amino-4,6-dichloro-s-triazine [31].

Figure 6. (a) SEM image of a film composed of aligned CNTs prepared in 1996. This film with a thickness of 50 μm was obtained by growing for 2 h. (b) High-resolution TEM image of a CNT composing the CNT film in (a), consisting of about 40 concentric shells of graphitic sheets with a sheet spacing of 0.34 nm. The inner and outer diameters of the tube are 4 and 34 nm, respectively. From W.Z. Li et al., Science, 274, pp. 1701–1703, 1996 [30]. Reprinted with permission from AAAS.

Figure 7. (a) Low-magnification SEM image of an MWCNT array grown by PECVD in 1998. (b) High-magnification SEM image of MWCNTs shown in (a). The CNTs are vertically grown on the substrate and the CNT sites are random. From Z.F. Ren et al., Science, 282, pp. 1105–1107, 1998 [32]. Reprinted with permission from AAAS.

Straight, well-aligned, and separated CNT arrays were not successfully fabricated until 1998 using a plasma-enhanced chemical vapor deposition (PECVD) method below 666°C (Figure 7) [32]. CNTs were aligned over areas up to several square centimeters on nickel-coated glass. The diameter and length of the aligned CNTs are controllable from 20 to 400 nm and from 0.1 to 50 μm, respectively. The CNTs were very straight (Figure 7(b)). Because the catalytic nickel nanoparticles were fabricated by radio frequency magnetron sputtering, the nanoparticles distributed randomly on the glass substrate. The vertical CNTs were then randomly grown on the glass surface.

Later, large periodic arrays of CNTs were grown by plasma-enhanced hot filament CVD on periodic arrays of nickel dots prepared by e-beam lithography [33] (Figure 8). The sites of the CNTs depend on the sites of catalytic nickel nanodots. The nanotube growth process is compatible with silicon integrated circuit processing, and CNT devices requiring freestanding vertical CNTs can be readily fabricated since then.

In order to obtain periodic catalytic nanoparticles cheaply, polystyrene microsphere lithography was developed [34,35]. Figure 9(a) shows aligned CNTs in a honeycomb lattice pattern. The CNTs grow from the periodically patterned catalysts prepared by microsphere lithography (Figure 9(b)). From then on, the vertically grown CNTs are site-controlled. These 3D-aligned CNTs have wide applications, such as field-emission displays, physical and biological sensors, etc.
At the same time, superlong CNT arrays were also grown vertically to the substrate surface using a thermal CVD method [36], especially the water-assisted CVD method.

Among the various CNT-related structures discovered, we mainly discuss here arrays of aligned CNTs which may be SWCNTs, DWCNTs, MWCNTs, and bamboo or fiber-like. Meanwhile, we recommend a handful of available books to interested readers for further reading and understanding on individual CNTs of more varieties [37–40].

1.2. Structures of CNTs

1.2.1. Graphite

A graphitic layer is a one-atom-thick planar sheet of sp²-bonded carbon atoms with a honeycomb crystal lattice structure (Figure 10(a)). The carbon–carbon bond length is 0.142 nm. Graphite layer is the basic structural element of CNTs. Its unique physical properties are reviewed in a collection of books and in a vast amount of literatures.

1.2.2. Single-walled CNTs

SWCNTs can be synthesized by CVD [6], arc discharge [11,12], and thermocatalytical disproportionation of carbon monoxide [42,43]. Now massive amount of SWCNTs is produced mainly
Figure 10. (a) An infinite graphite layer with \((n,m)\) nanotube naming scheme describing how a nanotube is rolled up. \(a_1\) and \(a_2\) are the unit vectors of graphite layer in real space. (b) SWCNT of zigzag structure, (c) SWCNT of armchair structure, and (d) SWCNT of chiral structure. C.N.R. Rao et al., Nanoscale 1, pp. 96–105, 2009 [41] – Reproduced by permission of The Royal Society of Chemistry.

by CVD methods. Most SWCNTs have a diameter close to 1 nm, with length extendable up to millimeter or even centimeter scales.

The structure of an SWCNT can be conceptualized by wrapping a graphitic layer into a seamless cylinder. Figure 10(a) shows how an SWCNT is rolled up from a graphitic layer. The way the layer is wrapped is represented by a pair of indices \((n,m)\) called the chiral vector. The integers \(n\) and \(m\) denote the number of unit vectors along two directions in the honeycomb crystal lattice of a graphitic layer. If \(n = m\), the SWCNTs are called armchair. If \(m = 0\), they are called zigzag, and the rest are called chiral.

SWCNTs have unique electrical properties. For a given \((n,m)\) SWCNT, if \(n = m\), the CNT is metallic with low energy properties of a Tomonaga–Luttinger liquid [44], and the rest of the SWCNTs can be either metallic or semiconducting depending on their chirality (or equivalently speaking, their diameter), as theoretically predicted [45–47] and experimentally confirmed [48,49]. The unique physical properties of SWCNTs are reviewed in various books [50] and literatures. For example, metallic CNTs can theoretically carry an electrical current density as high as \(4 \times 10^9\) A/cm\(^2\) which is more than 1000 times greater than good metals such as copper [51].

1.2.3. Double-walled CNTs
DWCNTs were observed during arc-discharge synthesis [1] and during the disproportionation of carbon monoxide [42]. The presence of DWCNTs was related to the nature of the
catalyst [52]. Now DWCNTs can be synthesized by CVD methods [53,54] and produced at gram scales [55].

DWCNTs are interesting members of the CNT family because their morphology and most physical properties are similar to those of SWCNTs, while their electrical and chemical properties are significantly improved for many application considerations. DWCNTs are especially important when functionalization is required to add new properties to the CNTs. In the case of SWCNTs, covalent functionalization will break some C-C bonds, leaving holes in the CNT structures and thus modifying both their mechanical and electrical properties. In the case of DWCNTs, only the outer walls are modified and therefore many properties are well preserved.

1.2.4. Multi-walled CNTs

The MWCNT structure (Figure 11) can be conceptualized by wrapping several graphite layers into a concentric seamless cylinder. There are two models, namely the Russian Doll model and the Parchment model [58], which can be used to describe the structures of MWCNTs. In the Russian Doll model, graphitic sheets are arranged in the form of concentric cylinders, for example, a (0,8) SWCNT within a wider (0,10) SWCNT. The inter-layer distance in an MWCNT is slightly above that in graphite, which is approximately 3.3 Å, suggesting a different layer-stacking mechanism. In the Parchment model proposed in 1960 [58] to explain the cylindrical structure of carbon fibers, a single continuous graphitic layer scrolls or rolls up to form concentric tubes.

1.2.5. Bamboo-like CNTs

Bamboo-like CNTs are usually synthesized using thermal CVD methods. They are usually produced at low gas pressures and high temperatures or at high gas pressures regardless of temperature [59,60]. As the pressure goes up, the wall and the inner diameter of the CNTs get thicker and larger, respectively, by increasing the number of graphitic layers. Once a layer forms in the bamboo-like structure, all the layers will terminate on the surface of the CNTs. Crystallinity of the bamboo-like CNTs usually becomes poorer with the increase in pressure due to higher growth rates. The inclination angle (the angle between the fringes of the wall and the axis of the CNT) increases with the pressure.

PECVD methods are also frequently employed to produce bamboo-like CNTs with even higher degree of deviations from the classic CNT structures. In some cases at low growth temperatures,
the structure is composed of closely stacked graphitic cups with very small hollow core or inner compartment space (Figure 12). The cross-sectional views of these PECVD-produced nanostructures look very much like fishbones [61] and are therefore occasionally called fishbone CNTs, or stacked-cup CNTs, or simply carbon nanofibers (CNFs) to ignore its low level of hollowness altogether. Note that these CNFs sometimes may also have concentric outer walls with a zero inclination angle in addition to the fishbone structures [63].

1.2.6. Other carbon nanomaterials
Besides the above carbon nanomaterials, there are other varieties, such as CNTY-junctions [23,24, 26,64,65], amorphous CNTs [66–70], coiled CNTs [71–73], CNT nanobuds [27], CNT rings [74–76], carbon microtubes [77], and carbon nano-onions [78,79]. The interested readers are referred to these references.

1.3. High anisotropic properties of CNTs
For an overview of the basic physical properties of SWCNTs, we refer the readers to some excellent books and review articles on electronic properties [50,80–86], structural properties [50,84,86], optical properties [40,50,85–88], electrical properties [40,50,86], thermal properties [40,85,86,89],
mechanical properties [40,83,86,90], atomic properties [40,86], magnetic properties [83,91], and vibrational properties [80].

Because of the anisotropic properties of graphite along \( a \)-plane and \( c \)-plane directions, the physical properties of CNTs are also anisotropic. The diameter of a CNT is several nanometers, while the length may be in millimeters even centimeters [92–94]. In these cases, the high aspect ratios of individual CNTs can go up to \( \sim 10^7 \), meaning a CNT can be macroscopic and nanoscopic at the same time. High aspect ratios further enhance the degree of anisotropy of CNT properties and also facilitate the construction of a macroscopic device that is easy to handle. The anisotropic properties and high aspect ratios make the aligned CNTs necessary in many applications.

1.3.1. Anisotropic mechanical properties

Simple geometrical considerations suggest that CNTs should be much softer in the radial direction than along the tube axis. Experimental Young’s modulus of SWCNTs is 1002 GPa [95] along the SWCNT axis (Figure 13). At the same time, TEM observation of radial elasticity suggested that even the van der Waals forces can deform two adjacent CNTs [96]. Nanoindentation experiments performed on MWCNTs indicated that Young’s modulus is in the order of several GPa, confirming that CNTs are indeed rather soft in the radial direction [97].

1.3.2. Anisotropic electrical properties

The electrical resistivity in the CNT axis direction is much lower than that in the radial direction. Figure 14 shows the electrical resistance along and perpendicular to the CNT tube axis. When the electrons travel perpendicular to the CNT tube axis, the electrons need to hop from one graphitic layer to another, causing a higher electrical resistivity.

1.3.3. Anisotropic thermal properties

All CNTs are expected to be very good thermal conductors along the axis direction, sometimes exhibiting ballistic transports, but are simultaneously good thermal insulators perpendicular to the CNT axis. Measurements show SWCNTs’ room-temperature thermal conductivity is about
3500 W/m/K (Figure 15) along CNT axis direction. The value is much higher than that of copper, a metal well known for its good thermal conductivity of 385 W/m/K.

1.3.4. Other anisotropic physical properties

Ellipsometry experiments of aligned MWCNT films indicated that the dielectric function parallel to the CNT axis resembles that of graphite parallel to the graphitic planes, while the dielectric function perpendicular to the CNT axis shows features characteristic of the dielectric function of graphite perpendicular to the graphitic planes [97].

Figure 16 shows the anisotropic magnetic susceptibility of CNTs. A calculation using the tight-binding model and the London approximation shows that the magnetic susceptibility $\chi$ is a sensitive function of the magnetic field direction $\theta$ [101]. Numerically, the $\theta$ dependence is
well approximated by a function $\chi(\theta) = a + b \cos(2\theta)$. Experiments also show that the magnetic susceptibility of CNT bundles is more diamagnetic when the magnetic field is parallel to the CNT axis than when the field is perpendicular to the CNT axis [102]. The magnetic behavior of CNT bundles is different from that of random CNTs [100].

1.4. Growth techniques of CNTs

CNTs have been synthesized by arc discharge, laser ablation, CVD, and flame synthesis. Most of these processes take place in vacuum or with process gases. CNTs can be produced in massive quantities, making them available to industrial-scale applications. Table 1 lists some synthesis methods. Below we will briefly discuss these techniques.

1.4.1. Arc discharge

The arc-discharge technique was first established to synthesize Buckminster fullerenes in 1985 [2]. Figure 17 shows a growth setup of arc discharge. During this process, the carbon contained in the negative electrode sublimates because of the high discharge temperature (above 1200°C). In 1991, the method was used by Iijima [1] who observed MWCNTs in the carbon soot of graphite electrodes using a current of 100A originally intended to produce fullerenes. Bulk quantities of MWCNTs

Table 1. Synthesis methods of CNTs.

<table>
<thead>
<tr>
<th>Method</th>
<th>Reaction temperature (°C)</th>
<th>CNT length (μm)</th>
<th>CNT growth rate (μm/s)</th>
<th>CNT yield</th>
<th>CNT quality</th>
<th>Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arc discharge</td>
<td>~ 4000</td>
<td>~ 1</td>
<td>Up to $10^7$</td>
<td>Low</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Laser ablation</td>
<td>RT–1000</td>
<td>~ 1</td>
<td>~ 0.1</td>
<td>Low</td>
<td>High</td>
<td>Med</td>
</tr>
<tr>
<td>Flame</td>
<td>500–1200</td>
<td>1–10</td>
<td>10–100</td>
<td>Low</td>
<td>High</td>
<td>Med</td>
</tr>
<tr>
<td>Thermal CVD</td>
<td>500–1200</td>
<td>0.1–10²</td>
<td>0.1–10</td>
<td>High</td>
<td>Med</td>
<td>Med–high</td>
</tr>
<tr>
<td>PECVD</td>
<td>100–800</td>
<td>0.1–10</td>
<td>0.01–1</td>
<td>Low</td>
<td>Low–med</td>
<td>Med</td>
</tr>
</tbody>
</table>
can be produced by this method under suitable arc-evaporation conditions [104]. After adding catalysts, SWCNTs were also produced [11,12] and sometimes even in large quantities [105].

The method has been most widely used for CNT synthesis because of the simple setup. The yield is up to 30% by weight and both SWCNTs and MWCNTs of lengths up to 50 μm can be produced. Industrially, the CNTs are usually separated from the amorphous carbon by-products through purification processes found in some review literatures [16,18,19] for SWCNTs [18] and MWCNTs [19]. The diameter and the length of the CNTs are hard to control because of the temperature nonuniformity and pressure instability issues [106]. The CNTs synthesized by arc discharge have very few structural defects and are quite straight. The method is reviewed in some books and papers [107,108].

Usually the arc-discharge-produced CNTs are random. Recently, it was reported that self-aligned CNTs were synthesized [109] in the soot deposited at the carbon cathode by a DC arc-discharge method using copper catalysts.

1.4.2. Laser ablation
Laser ablation is a process of removing materials from a solid surface by irradiating the surface with a laser beam. At low laser flux, the material is heated by the absorbed laser energy and evaporates or sublimes.

Laser ablation was developed in 1995 to produce CNTs [21,111]. Figure 18 illustrates the growth setup of laser ablation. In a typical laser ablation process for CNT growth, the graphite block is placed inside an oven and hit by a pulsed laser, and Ar gas is pumped along the direction of the laser point. The oven temperature is set approximately to 1200°C. As the laser ablates the target, carbon is vaporized and carried by the flowing gas onto a cool copper collector. CNTs grow on the cooler surfaces of the reactor as the vaporized carbon condenses. Sometimes, a water-cooled surface may be included in the system to collect the CNTs. SWCNTs are formed from a composite block of graphite and metal catalyst particles [21], whereas MWCNTs form from pure graphite as the starting material [111]. Growth mechanisms for CNTs in a laser-ablation process can be found in the literature [112]. It is proposed that the laser heats and vaporizes the target surface containing graphite and catalytic metal (nickel and cobalt). As the vaporized species cool, small carbon molecules and atoms quickly condense to form larger clusters, including
possibly fullerenes. The catalysts also begin to condense, but more slowly at first and attach to carbon clusters preventing their closing into cage structures. From these initial clusters, tubular molecules grow into SWCNTs until the catalyst particles become too large, or until conditions have cooled sufficiently down that carbon no longer can diffuse through or on the catalyst particles. It is also possible that the particles become completely coated with a carbon layer such that no more carbon atoms can be absorbed and therefore nanotube growth ceases.

The laser ablation method yields around 70–90 wt% CNTs in the growth product. Compared to arc discharge, the diameter of the laser-ablation-produced CNTs can be better controlled by the reaction temperature. However, laser ablation is more expensive than either arc discharge or CVD due to the need for high-power lasers. Ordered CNT bundles (Figure 5) can also be synthesized using this method.

Besides laser heating, other heating methods can also be employed, such as using an electron beam to evaporate graphite blocks in high vacuum to grow CNTs [113] or to evaporate ultrathin graphite foils in ultrahigh vacuum [114].

1.4.3. Chemical vapor deposition

CVD is a chemical process used to produce high-purity, high-performance solid materials. The process is often used in the semiconductor industry to produce thin films.

The catalytic vapor-phase deposition of carbon was first reported in 1959 using carbon monoxide–hydrogen mixtures over Fe [115]. In 1993, CNTs were synthesized by this process from acetylene over Fe particles at 700 °C [116]. Large-scale aligned CNTs were synthesized by thermal CVD catalyzed by iron nanoparticles embedded in mesoporous silica [30]. The aligned nanotubes are approximately perpendicular to the surface of the silica and form an aligned array of isolated tubes with inter-tube spacings of about 100 nm (Figure 19(a)). The growth direction of the nanotubes may be controlled by orientation of the pores from which the nanotubes grow (Figure 19(b)).

Later, the method was employed to grow CNT arrays on glass under the assistance of plasma [32]. Large-scale CNT arrays are well synthesized (Figure 20). Up to now, this PECVD process
Figure 19. CNT array grown by thermal CVD method. (a) High-magnification SEM image of CNTs growing out from the mesoporous iron/silica substrate and forming an array. (b) Possible growth model of CNTs formed on iron nanoparticles embedded in mesoporous silica. From W.Z. Li et al., Science, 274, pp. 1701–1703, 1996 [30]. Reprinted with permission from AAAS.

Figure 20. SEM micrograph of CNTs grown by DC PECVD on glass. From Z.F. Ren et al., Science, 282, pp. 1105–1107, 1998 [32]. Reprinted with permission from AAAS.

has become one of the most popular methods to synthesize CNTs and CNT arrays on various substrates.

In the CVD process, the catalyst is one of the key factors for CNT growth. Nickel, cobalt, stainless steel [117,118], gold, platinum, and many alloys have been successfully used as catalysts. Discussions on the formation mechanism for catalytically grown CNTs can be found in the literatures [6,71,119–124], including bulk diffusion mechanisms [123,124], surface diffusion mechanisms [6], spatial velocity hodograph [71] and catalyst surface step edge effects [120]. There also exists a two-step growth mechanism: the first step corresponding to the catalytic growth of a CNT and the second step corresponding to a thickening step via a catalyst-free pyrolytic carbon deposition mechanism [125–129].

1.4.4. Other methods

Hydrothermal. In the previous methods, high reaction temperatures and metal catalysts are always needed. The hydrothermal method is capable of synthesizing CNTs at lower temperatures. It is reported that CNTs were synthesized from polyethylene, ethylene glycol, and other sources with or without catalysts under hydrothermal conditions at 700–800°C [130,131], by a ethanol thermal reduction process using magnesium in a stainless autoclave at 600°C [132], from hexachoroberzenone or tetrachloroethylene in the presence of Co/Ni catalyst at 350°C [133], by a solvothermal approach at 310°C [134], by reducing ethyl alcohol with NaBH₄ in a high concentration/strong basic solution at 180°C [135], from CCl₄ using iron-encapsulated polypropyleneimine dendrimers as a catalyst in supercritical carbon dioxide medium at 175°C [136],
Advances in Physics

Figure 21. CNTs synthesized by hydrothermal method. (a) SEM image of CNTs and (b) HRTEM image of a CNT. Reprinted with permission from W. Wang et al., Journal of the American Chemical Society, 127, pp. 18018–18019, 2005 [62]. Copyright (2005) American Chemical Society.

from ethyl alcohol/polyethylene glycol in a basic aqueous solution with high concentration of NaOH at 160°C without the addition of catalyst of Fe/Co/Ni [137], and from hydrothermal method at autogenic pressure [138]. The synthesized CNTs are MWCNTs or SWCNTs. The CNTs usually graphitized well (Figure 21). It is worth noting that the diameters of the as-prepared MWCNTs by the low-temperature hydrothermal route are much smaller than those prepared by high-temperature hydrothermal methods [131].

**Flame method.** In addition to the above-described state-of-the-art techniques used in the laboratories, CNTs are commonly formed in such mundane places as ordinary flames, produced by burning methane, ethylene, and benzene, found in soot from both indoor and outdoor air in the natural, incidental, and controlled flame environments. Curved CNTs have been found in the bricks of blast furnaces at 450°C from carbon monoxide [139]. It was reported that CNTs were discovered in ancient Damascus sabers forged more than 400 years ago [10]. However, these naturally occurring varieties can be highly irregular in size and quality because the environment in which they are produced is often highly uncontrolled. Recently, uniform CNTs [140], such as MWCNT arrays [141] and SWCNT arrays [142], are produced in controlled flame environments.

**Disproportionation of carbon monoxide.** As discussed in Section 1.1, the first probable CNTs published in 1952 were synthesized by this method [5]. Later, hollow MWCNTs [7] as well as SWCNTs [42] were produced by catalytic disproportionation of carbon monoxide.

**Catalytic pyrolysis of hydrocarbons.** Pyrolysis is an old method to grow CNTs. As we discussed in Section 1.1, carbon filaments were produced by the thermal decomposition of methane before 1900 [4] and CNTs were probably synthesized through benzene decomposition in 1976 [6]. Pyrolytic CNT growth mechanism was described in some literature [125].

**Electrolysis.** CNTs can also be prepared through electrolysis in molten alkali halide salts [143,144]. More details of the synthesis of CNTs are found in the review literatures and related books [88,145,146].

2. Technologies to achieve CNT alignment

Because of the strong anisotropy of CNT properties, it is almost always necessary to consider the orientation of its longitudinal direction when a CNT component is considered for both scientific studies and practical applications. Knowing the orientation is also a prerequisite to locate the
two ends of a CNT that usually needs to be physically contacted by instrumental probing during characterizations or device integration. For a group of CNTs, the anisotropic nature of individual CNTs is best preserved and explicitly conceived when all the CNTs are aligned in the same direction as an array. Also as opposed to many random CNT ensembles where individual CNTs are frequently bundled and twisted around one another, aligned CNT arrays usually are composed of isolated straight individual CNTs, making it possible to control the morphology of each of them, the spatial arrangement among them, the uniformity across the entire array, etc. This degree of detailed control is critically required for many major applications in electronics, optics, and others.

There are a handful of experimental technologies available to align a single or an array of CNTs along a pre-determined orientation. The techniques rely on different mechanisms and therefore are applicable to different situations. These techniques are categorized into two groups pertaining to when the alignment is achieved: (a) in situ techniques where alignment is achieved during the CNT growth process and (b) ex situ techniques where CNTs are originally grown in random orientations and alignment is achieved afterwards such as during the device integration process. Such a choice is not out of absolute necessity but it emphasizes those differences between the two schemes that are more important for potential large-scale manufacturing. While in situ techniques bear the benefit of straightforwardness and simplicity, ex situ techniques are free of growth restrictions such as substrate material and temperature. As process simplicity always comes first by the consideration of a manufacturer, the majority alignment techniques invented so far are in situ.

2.1. In situ techniques for CNT alignment

In situ techniques directly align CNTs during the CNT growth process. It is straightforward and simple. Up to now, aligned CNTs are most frequently grown using the in situ techniques of thermal CVD and PECVD assisted by catalytic nanoparticles.

2.1.1. Thermal CVD with crowding effect

In a catalytic CVD growth process, CNTs are grown from catalyst nanoparticles deposited on a substrate. One of the most common scenario is that the nanoparticles are formed through a solid-state dewetting process [147,148] of a continuous polycrystalline thin film deposited by physical vapor deposition (sputtering, evaporation, etc.). When a thin film of catalytic material (such as Fe) is heated under a non-reactive gas ambient or vacuum, voids will first appear at grain boundary triple junctions and grow larger driven by surface energy minimization. According to the Rayleigh instability theory [149], the continuation of such a dewetting process will lead to fingering morphology at the void rims and edges of the film and eventually result in isolated particle formation with both particle size and spacing determined by the film thickness. For CNT growth by CVD, catalytic nanoparticle size is usually only 0.5–10 nm, which requires very thin starting catalyst films and consequently very tight particle spacing. As CNTs begin to grow from these densely distributed catalyst particles, it is generally conceived that van der Waals forces among close-by CNT neighbors cause them to all grow vertically to the substrate. Indeed, when certain growth conditions lead to a low growth yield, i.e., CNTs only grow from a small fraction of all the catalyst particles, the decrease in CNT site density (or increase in CNT spacing) results in complete randomness of CNT orientations [150], which confirms the crowding effect as the alignment mechanism for densely packed CNT arrays. Besides the thin-film dewetting technique to obtain high-density catalyst particles, there are other ways to deposit pre-prepared catalyst nanoparticles at a high density onto growth substrates such as solution-based techniques [151], sublimation techniques [152], and deposition techniques [153]. As long as the CNTs are grown at a high enough areal density with a tight spacing, crowding effect will be effective to ensure vertical alignment of all individual CNTs.
Since catalyst particles prepared by dewetting of thin films from physical vapor deposition usually have small inter-particle spacing, the task to achieve aligned CNT growth solely relies on high growth yield by optimal CVD growth control. Such high yield growth has been repeatedly achieved throughout the CNT research community, for SWCNTs [92,150], DWCNTs [154], and MWCNTs [155], and the wall number control is a complicated topic including factors of catalyst particle size, growth conditions, etc. which are not the intended focus of this review. The key to realize high yield growth is a proper introduction of oxidative agents (O\textsubscript{2}, H\textsubscript{2}O, etc.) under the gas ambient so that the catalyst particle surfaces remain active for the longest possible period, which is presumably achieved by balancing the competition between amorphous carbon growth and sp\textsuperscript{2} graphitic crystal formation on the catalyst particles. Oxidants can not only remove or prevent amorphous carbon growth, but may also etch into graphite layers when used at higher than favorable concentrations. Another important function of oxidants is to remove excessive H\textsubscript{2} which is found to have negative effects on CNT growth during the incubation stage [150]. Controlling the proper level of oxidants in the growth environment depends on the specific deposition apparatus configuration and in some cases the timing and duration of oxidant introduction. When alignment is achieved, it is possible to grow aligned arrays of very long CNTs up to multiple millimeters (Figure 22) as the growth front is kept unblocked [156], not possible in the case of unaligned growth.

If the starting catalyst thin film is patterned, aligned CNTs can grow into interesting vertical bundles with pre-designed shape and coordinate. Also, because such an aligned growth is independent of the substrate macroscopic morphology, one can use shaped substrates to obtain CNT arrays oriented in different directions according to local substrate surface curvature. Figure 23 shows SEM images of CNT arrays with different shapes. These CNT arrays are aligned by crowding effect during thermal CVD.

CNT arrays can also be grown on micron-sized substrates using the crowding effect. The nanobrush shown in Figure 24 demonstrated the versatility of this crowding effect method with various substrate surface geometries, as long as the catalyst particle spacing and high yield growth conditions are met.

In addition, there are so-called “regrowth” techniques where one aligned CNT array as a layer of thick microscopic forests can be grown on top of another [157,158] with the top array having its spacing and alignment inherited from the bottom one (Figure 25). A series of multiply stacked nanotube towers are selectively grown on SiO\textsubscript{2} substrate with Au patterns. The vertically aligned nanotube arrays are perfectly stacked on top of one another, each grown on the substrate via CVD and vapor-phase catalyst delivery. During the growth, each layer, consisting of uniformly aligned arrays of hundreds-of-microns-long multi-walled nanotubes, nucleates and grows from the buried original substrate plane (silicon oxide) even after the substrate gets completely covered by continuous and multiple layers of nanotubes deposited during previous growth sequences. In order for this to happen, it is imperative that the hydrocarbon and the catalyst metal precursors diffuse through several hundreds of microns of porous nanotube films and start growing on top of the buried substrate, underneath the bottom of the multilayered stack of nanotubes. It also means that, every time a fresh layer is nucleated and grown from the bottom, the rest of the layers in the stack get lifted up from the substrate, moving up with the freshly growing nanotubes, from the bottom-up.

2.1.2. Thermal CVD with imposed electric fields

Since CNTs are all electrically conductive (although with varying conductivities), a growing CNT under an external electric field can be treated as an induced electric dipole having a tendency to align with the electric field lines. Various methods have been developed to apply a strong enough electric field during the CNT growth process to achieve uniform alignment of CNTs based on this principle. Such field-directed growth is a useful technique to organize CNTs into horizontally aligned arrays.
Figure 22. SWCNT forest grown with water-assisted CVD. (a) Optical image of a 2.5–mm tall SWCNT forest on a 7 × 7 mm silicon wafer. (b) SEM image of the same SWCNT forest. (c) SEM image of the SWCNT forest ledge. Scale bar: 1 μm. (d) Low-resolution TEM image of the nanotubes. Scale bar: 100 nm. (e) HRTEM image of the SWCNTs. Scale bar: 5 nm. From K. Hata et al., Science, 306, pp. 1362–1364, 2004 [92]. Reprinted with permission from AAAS.

Electric fields can orient CNTs owing to their large and highly anisotropic polarizability [160]. Figure 26(b) shows parallel CNTs directed by an electric field between a pair of electrodes on a dielectric substrate [159]. In the absence of an electric field, the CNTs grow into random CNT networks (Figure 26(a)). SWCNTs can be field directed along the field direction above 0.13 V/μm DC field strength or above 0.25 V/μm AC field strength. Highly aligned suspended SWCNTs can be grown under field strength in the range of 0.5–2 V/μm [159].

The field-alignment effect originates from the high polarizability of CNTs. The electric field $E$ produces a dipole moment $P$ on a CNT, that is, $P = \alpha E$. The polarizability along the tube axis $\alpha_\parallel$ is much higher than that perpendicular to the tube axis $\alpha_\perp$ [160]. For a nanotube oriented at an angle $\theta$ with respect to $E$, the dipole moment of the nanotube is along the tube axis with $P = \alpha_\parallel E \cos \theta$. The torque on the dipole moment is $\tau = |P \times E| = \alpha_\parallel E^2 \sin \theta \cos \theta$. Correspondingly, a force is applied to the dipole to rotate and align the tube with $E$ (inset in Figure 26(b)). Calculation indicated that the induced large dipole moments lead to large aligning torques and forces on the CNT and totally prevent randomization of nanotube orientation by thermal fluctuations when the electric field $E$ is $\geq 0.5 \text{ V/μm}$ and the length of CNT is about 20 μm at 900°C [159].
Figure 23. SEM images of vertical CNT arrays with various shapes. (a) Molecular O$_2$-assisted growth of vertical SWCNT square and circular towers. (b) CNT tower CVD synthesized on 38 $\mu$m $\times$ 38 $\mu$m catalyst patterns. (c) SWCNT cylindrical pillars with 150 $\mu$m radius, 250 $\mu$m pitch, and 1 mm height, grown by water-assisted CVD on patterned catalyst. Inset: SEM image of a root of a pillar. Scale bar: 50 $\mu$m. (d) SWCNT sheets with 10 $\mu$m thickness, grown by water-assisted CVD on catalytic stripe patterns. (a) Reprinted with permission from G. Zhang et al., Proceedings of the National Academy of Sciences, 102, pp. 16141–16145, 2005 [150]. Copyright (2005) National Academy of Sciences, USA. (b) From S. Fan, et al., Science, 283, pp. 512–514, 1999 [36]. Reprinted with permission from AAAS. (c) From K. Hata et al., Science, 306, pp. 1362–1362, 2004 [92]. Reprinted with permission from AAAS.

The grown CNTs suspend across the electrodes [159] or lie on the substrate surface [161, 162]. Two important factors control the aligned growth of CNTs on substrates. The first is the aligning ability of the electric field. For a 10 $\mu$m SWCNT, a 1 V/$\mu$m field strength would induce a dipole of 10 Debye, sufficient to overcome most of the orientation randomizing forces such as thermal vibration [159]. Besides the external electric field, the local electric field caused by static charging can also orient the CNTs grown by CVD [163]. For example, when aluminum nano-islands are patterned on oxidized silicon substrates, a large electric field can be created by surface charging in the hot, reactive conditions of the CVD growth, and/or by an unbalanced charge at the alumina/oxide interface. Negative charge densities as high as 7 x 10$^{12}$ electron/cm$^2$ can be produced at the alumina/oxide interfaces [164]. CNTs grow on the silicon oxide surface near an alumina boundary, orienting perpendicularly to the boundary. Another factor is strong van der Waals interaction between the CNT and the substrate. It is believed that during growth and lengthening of CNTs, the nanotubes stay away from substrate surfaces and the nanotubes fully experience the aligning effect of the electric field. CNTs do not contact the substrate surface until CNTs have been fully aligned to the electric field and guided onto the substrate surface. It is observed that field-directed CNTs suspend over quartz substrate [159] while lying on the SiO$_2$/Si
substrate surface [161]. The thermal vibration and the feeding gas effects are negligible compared with the strong electric force [159].

The orientation of the aligned CNTs is mainly dependent on the length of CNTs and the electric field besides the thermal randomization and van der Waals forces. The thermal vibration and the effect of feeding gas are negligible compared with the strong electric forces [159]. Under a certain electric field strength, the longer the CNTs, the better the alignment [159]. A statistical analysis of the nanotube orientation indicates that the direction of the aligned CNT axis is not parallel to the electric field perfectly, but slightly deviates by several degrees off the direction of the electric fields [162].

Plasma in the PECVD process also induces a self-biased electric field imposed on the substrate surfaces. The induced local electric fields can also direct the CNT growth to align along local electric field directions in DC PECVD [165] and microwave PECVD [166] processes.

Field-directed growth has been employed to grow SWCNTs between electrodes to produce self-assembled field-effect transistors.
Attempts to organize CNTs into 2D crossbar structures by electric field-directed growth in two dimensions have also been carried out [167,168]. The crossbar structure of CNT alignment is hard to obtain only through electric fields. Usually, CNT crossbar architectures are achieved by combining field-directed growth with surface-directed growth [169] (see Section 2.1.5.4). 2D SWCNTs have successfully been produced along faceted nanosteps and along electric field in CVD growth. The electric field-directed CNTs are perpendicular to the surface-directed CNTs. The two alignment mechanisms take place simultaneously, producing dense nanotube grids.

2.1.3. Vertically aligned CNT arrays by PECVD

CNT arrays have been in situ fabricated more successfully by the PECVD method. The CNT arrays in situ aligned vertically were first synthesized using DC-PECVD [32,170–172]. Later a variety of PECVD methods, such as RF-PECVD, hot-filament PECVD, microwave PECVD, electron cyclotron PECVD, etc., are developed to grow aligned CNTs. DC-PECVD is discussed in
detail in Section 3, including the experimental setup and experimental conditions. Other PECVD methods are largely similar to the DC-PECVD method.

In these PECVD processes, DC electric fields, radio-frequency electric fields, or microwaves produce plasmas to primarily lower the synthesis temperature of CNTs. At the same time, an electric field (DC or AC) is also produced over the substrate surface, directing the CNT growth similar to the electric field effect discussed in Section 2.1.2. The straight CNTs grow along the direction of the parasitic electric field in the plasma [165,166].

Besides the CNT alignment along the plasma-induced electric field, CNTs can also be arranged on the substrate surface to form 3D CNT arrays. The sites of catalytic nanoparticles are critical to the location of CNTs on the substrate surface. Because the CNTs grow only from the catalytic nanoparticles in a PECVD process, the sites of catalytic nanoparticles determine spatial locations of CNTs. So the preparation of catalytic nanoparticles is very important on the fabrication of vertical CNT arrays of various patterns. Table 2 summarizes several methods for preparing catalytic nanoparticles.

### 2.1.3.1 One-dimensionally ordered CNT arrays

Usually the PECVD-grown CNTs are one-dimensionally (1D) ordered: the aligned CNTs are vertical to the substrate surface, while the CNT

<table>
<thead>
<tr>
<th>Methods</th>
<th>Position</th>
<th>Size</th>
<th>Site density</th>
<th>Procedure</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
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<td>Simple, easy</td>
<td>Cheap</td>
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<tr>
<td>Sputtering deposition</td>
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<td>Controllable narrow</td>
<td></td>
<td>Easy</td>
<td></td>
</tr>
<tr>
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<td>Narrow</td>
<td>Controllable</td>
<td>Time consuming</td>
<td>Expensive</td>
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<td>Controllable</td>
<td></td>
<td>Less than three patterns</td>
</tr>
<tr>
<td>Microsphere lithography</td>
<td>Controllable</td>
<td>Controllable</td>
<td>Controllable</td>
<td></td>
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</tr>
<tr>
<td>e-beam</td>
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<td>Controllable</td>
<td>Controllable</td>
<td>Expensive</td>
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</tr>
<tr>
<td>Micro-stamp</td>
<td>Controllable</td>
<td>Controllable</td>
<td>Controllable</td>
<td></td>
<td>One pattern</td>
</tr>
</tbody>
</table>

Table 2. Some preparation methods of catalytic nanoparticles.
sites are random because of the random locations of catalytic nanoparticles on the substrate. The catalytic nanoparticles can be prepared by many methods, such as solution method [173–176], sputtering deposition [32,154,177], and electrochemical deposition [178]. The average number of catalytic nanoparticles per unit area can be controlled while the site locations of the nanoparticles remain random on the substrate surface.

**Solution method.** Solution method is the simplest way for producing catalysts while also widely employed in preparing catalysts for various nanowire growths. Usually the substrate is soaked in the catalytic compound, water or alcohol solution (such as NiNO₃ solution), for several minutes and then dried at room temperature. The deposited ions or ion clusters work as catalysts. In some cases, the deposited catalyst particles are reduced in hydrogen to activate their catalytic activity. CNTs are grown from these catalysts. The catalysts prepared by the solution method randomly distribute on the substrate surfaces and the PECVD-grown CNTs are 1D ordered along the plasma-induced electric field.

For example, iron catalysts have been prepared by this method. Iron nanoclusters with diameters between 3 and 13 nm were synthesized in organic solvents by thermal decomposition of iron pentacarbonyl and then were deposited onto a silicon substrate [173]. Iron oxide nanoparticles with diameters of 1–2 nm were synthesized by soaking silicon oxide substrates in a solution of hydroxylamine and FeCl₃ [174]. Iron catalysts were also prepared by the iron-storage protein, ferritin [175], and by the polystyrene-block-polyferrocenyldimethylesilane diblock copolymer [176]. 1D CNT arrays were successfully grown from these catalysts.

**Sputtering deposition.** Sputtering (magnetron) deposition is usually employed to coat thin films on substrates and now is one of the most commonly used methods to synthesize the surface arrays of metal particles. The sputtered film is usually continuous at a thickness above 1 nm. Such as-coated films are not good catalysts for CNT growth. However, the continuous films are always coarsened into discrete nanoparticles under annealing or through a solid-state dewetting process. So-prepared nanoparticles are usually well capable of catalyzing the growth of CNTs.

The catalyst preparation procedure of sputtering is simple and effective to grow catalytic nanoparticles for the growth of vertically aligned CNTs [32,154,177]. Up to now, catalytic nanoparticles have been DC magnetron sputtered or radio frequency sputtered on substrates. Although this method is straightforward, it offers little control over the size or spacing of the metal nanoparticles, and patterned nanoparticle arrays are not achievable this way without additional modifications such as templating.

In a typical DC magnetron sputtering process, substrates are cleaned in alcohol by ultrasonication first, and then loaded into the sputtering chamber for catalyst film deposition. The chamber is evacuated to a base pressure of $5 \times 10^{-7}$ to $3 \times 10^{-6}$ Torr. Then the pressure is maintained at 3–6 mTorr by introducing Ar gas. The catalyst target is Ar⁺ bombarded for a few minutes to remove the oxidized surface layer on the target. Then the substrate temperature is maintained at 0–300°C during deposition. The sputtering normally takes a few seconds to about 20 min to achieve catalyst film thickness of 2–100 nm.

The thickness of the sputtered films is usually in the range of 2–100 nm. The as-deposited films are normally smooth and continuous.

In order to enhance the catalytic activity, the as-sputtered films are always annealed at high temperature before CVD growth. The annealing is usually carried out in the same CVD chamber for CNT growth. The catalyst-coated substrates are loaded into the chamber, then the chamber is pumped down to about 1 mTorr or less, followed by heating to several hundred Celsius degrees. If the catalyst films have been exposed to air, annealing in hydrogen may remove the oxidized surface layer on the catalyst films. Depending on the annealing temperature and time, the continuous film develops into many individual nanoparticles, as shown in Figure 27. Statistical analysis of nanoparticle sizes indicates the catalyst nanoparticle size increases linearly with the increase
of the sputtered film thickness when it is below 100 nm, as theoretically predicted by Rayleigh instability theory.

Aligned CNTs are usually grown by PECVD methods immediately after the annealing step. During the PECVD growth, the plasma intensity should be well controlled for optimal results. If not, those catalytic nanoparticles would either be quickly knocked off the substrate (over-etched) or agglomerate (over-heated) into bigger ones to survive.

In order to grow isolated aligned CNTs, discrete catalytic nanoparticles shown in Figure 28(c), not adjacent ones shown in Figure 28(a) and (b), are needed. Otherwise, more than one CNTs will grow closely together forming CNT bundles as shown in Figure 28(d) and (e). In order to obtain uniform and isolated catalysts, the as-prepared catalysts can be pre-etched by a plasma before introducing carbon sources.

Electrochemical deposition. Electrochemical deposition has been employed to prepare Ni \[170,178,181\], Ag \[182–184\], Au \[184\], and Pt \[185\] catalytic nanoparticles with different nucleation site densities and different particle diameters for CNT array growth. Similar to the catalysts prepared by the sputtering method, the electrochemically deposited nanoparticles are also random. The site density and diameter of catalytic nanoparticles can be adjusted straightforwardly. Compared with the sputtering methods, the electrochemically deposited metal nanoparticles could have a lower site density, smaller sizes, more uniform diameters, and can be well controlled. For Ni catalytic nanoparticles, the site density can be easily tuned between about \(10^6\) and \(10^8\) cm\(^{-2}\) and the diameter can be finely tuned from less than 50 nm up to 200 nm \[178,186\]. Figure 29 shows the CNTs with different site densities from different catalytic site densities.

The electrochemical deposition of catalytic nanoparticles is a cheap, effective technique, and is scalable to tens of inches in surface distribution dimension. The CNT arrays grown from catalysts prepared by electrochemical deposition are therefore also inexpensive and scalable although the CNTs are randomly arranged on the substrate surface.
2.1.3.2 Three-dimensionally ordered CNT arrays

In order to synthesize 3D ordered CNTs, 2D ordered catalytic nanoparticles are required. The 2D ordered catalytic nanoparticles can be prepared by photolithography, X-ray photolithography, e-beam lithography [36,187], microsphere lithography, anodized aluminum oxide (AAO) templating [141,188,189], and micro-stamp method [190]. Among them, the microsphere lithography technique is a simple, cheap, and effective method to produce 2D ordered catalytic nanoparticles in inch-scale. After the 2D catalytic nanoparticles are prepared, the CNTs are vertically grown from them using PECVD method to form 3D CNT arrays.

Microsphere lithography. Microsphere lithography has been proved to be a very simple, economic, and effective technique to fabricate large-scale nanoparticle arrays with long-range periodicity [34,35,191–194]. It utilizes submicron latex beads hexagonally arranged into a monolayer as a shadow mask for the following evaporation of various materials. As-deposited catalytic nanoparticles have a quasi-triangular shape, caused by the aperture shape in the microspheres.
The microsphere lithography process involves three main steps [191,193,195]. Firstly, a 2D self-assembled and periodically ordered monolayer of microspheres is formed on a substrate surface (Figure 30(a)). Several drops of the microsphere suspension are applied to the surface of a substrate and then spread using a pipette tip. After being held stationary for about 1 min to obtain good dispersion of the suspension, the substrate is then slowly immersed into a pond of deionized water. Once the microsphere-coated surface is immersed, microspheres lift off from the substrate and form an unordered monolayer floating on the water surface. Then, a few drops of 2% dodecylsodiumsulfate solution are added to the water surface to change the surface tension (surface tension of water is 72.8 dynes/cm² at 20°C, while that of sodium dodecylsulfate solution is 40–70 dynes/cm² [197]). After the surface tension is reduced, all microspheres immediately assemble into a close-packed monolayer. At the same time, the monolayer is pushed aside due to the change in the surface tension. The prior substrate is then removed through a clear area. Then the microsphere monolayer is picked up by another clean substrate that is then slowly dried.

Figure 29. SEM images of CNT arrays grown on Ni nanoparticles deposited electrochemically with a site density of (a) $7.5 \times 10^5$ cm$^{-2}$, (b) $2 \times 10^6$ cm$^{-2}$, (c) $6 \times 10^6$ cm$^{-2}$, (d) $2 \times 10^7$ cm$^{-2}$, (e) $3 \times 10^8$ cm$^{-2}$, and (f) a freestanding CNT. Reprinted with permission from Y. Tu et al., Applied Physics Letters, 80, pp. 4018–4020, 2002 [178]. Copyright (2002), American Institute of Physics.

mask, and their size is tunable by the use of different sphere diameters. The technique has been used to prepare 2D catalytic nanoparticles to grow 3D CNT arrays [34,35], to prepare 2D ordered catalyst patterns for ZnO nanorod arrays [195], and to grow TiO$_2$ nanobowl arrays [196].
Figure 30. Highly ordered monolayer of polystyrene microspheres (diameter 0.5 μm) on a Si substrate made by the self-assembly microsphere lithography. (a) AFM image of the closely packed hexagonal microspheres. (b) Optical image of a Si substrate coated with microspheres. Reprinted with permission from K. Kempa et al., Nano Letters, 3, pp. 13–18, 2003 [35]. Copyright (2003) American Chemical Society.

Figure 30(a) shows a monolayer of polystyrene microspheres deposited on a 10 mm × 10 mm Si substrate. The uniform diffraction color in Figure 30(b) shows that the coated microspheres are indeed highly ordered without major defects over a long distance. This is further confirmed by a fast Fourier transform analysis. The area of a single domain can reach a few square centimeters.

Secondly, the microsphere monolayer is subsequently used as a shadow mask for physical vapor deposition of the catalyst (Fe, Co, or Ni). During this deposition process, the metal vapor can go through apertures in hexagonally packed microspheres leading to a honeycomb lattice array of quasi-triangular particles. Various deposition techniques such as e-beam lithography, magnetron sputtering, and thermal evaporation can be used to deposit metal catalysts through the microspheres. During a sputtered process, the isotropic velocity of the adatoms results in catalysts covering all opening areas, even beneath the microspheres. Therefore, after removing the microspheres, the sputtering technique usually produces a honeycomb-like catalyst network. During a thermal evaporation process, the deposition is line-of-site and the catalytic material is only deposited onto the areas of the substrate that are not shadowed vertically by the microspheres. After mask removal, a highly ordered hexagonal array of catalyst particles is formed on the substrate.

Thirdly, the microspheres are chemically etched away in toluene or tetrahydrofuran or mechanically by ultrasonication, leaving a patterned catalyst array on the substrate surface. Figure 31(a)
shows the triangular particles exposed after microsphere mask removal. The inter-particle spacing can be adjusted by adopting microspheres of different diameters.

After the 2D catalyst arrays are prepared, 3D ordered CNT arrays can be grown from them using PECVD methods, as shown in Figure 31(b).

2.1.4. **Thermal CVD growth under gas flow fields**

When CNTs grow at high temperatures, a feeding gas mixture (including reactive gases such as C_2H_4 and carrying gases such as H_2) passes over the growing CNTs. The feeding gas produces a flow field, causing CNTs to move along the direction of the gas flow. So the flow field caused by the feeding gas can orient the CNTs along the flow direction.

There are two key components in the alignment mechanism. Firstly, the growing fronts of nanotubes should be free above the substrate surface. This may happen due to buoyant effect or by fast-heating method, or at elevated sites over the substrate ground-level surface. Secondly, there should be a gas flow field to direct the CNT growth. A flow field always exists in the CNT growth processing by CVD. Once the flow gas can carry CNTs (or their growing fronts) to overcome gravity, CNTs will grow along the gas flow direction.

2.1.4.1 **Fast heating under high gas flow**

The flow-directed method is first employed to orient CNTs in a fast-heating CVD process [198–201]. Si wafer substrates with catalysts were heated quickly to the reaction temperature in a CVD reaction chamber. Some resulting CNTs are long and oriented, while the short ones are random in orientation. The orientation of the long nanotubes is controlled by the gas flow direction.

It is believed that the fast-heating process causes a convection of the gas flow due to the temperature difference between the substrate and the feed gas. Such a convection flow of the feed gas lifts the nanotubes upward and keeps them floating and waving in the feed gas until CNTs are caught by the substrate because of van der Waals forces. During the whole growth process, the nanotubes are floating in the feed gas and growing along the gas flow direction.

In the fast-heating growth process, the flow rate is typically about 1000 sccm [201]. Such a high-rate flow would cause local flow turbulences. The stability of the gas flow depends on the inner diameter \( \phi \) of the quartz tube of the CVD furnace and the gas flow speed \( v \), and can be characterized by the Reynolds number \( Re = \rho v \phi / \gamma \), where \( \rho \) is the density and \( \gamma \) the viscosity coefficient of the feed gas. The turbulent flow causes some CNTs to touch the substrate surface and terminates the CNT growth, producing short CNTs. The long CNTs are well oriented along the flow direction. So the synthesized CNTs in a fast-heating growth usually consist of well-oriented long CNTs and short ones that are randomly oriented as shown in Figure 32(a) [198]. At a higher Reynolds number, such as in the case of a large-diameter quartz tube and a high flow rate, relatively short and disordered CNTs are produced [202].

In order to grow long CNTs with alignment, a stable laminar gas flow is required to stabilize the catalytic tip of the growing CNTs, making CNT tips travel longer distances over the substrate surface. When using a small-diameter quartz tube and a low flow rate (such as less than 200 sccm), the Reynolds number can be reduced down to 50, near the lower limit of conventional laminar flow ranges. Better aligned CNTs can be achieved at low laminar flow rates (Figure 32(b)). Stable laminar flows with low Reynolds numbers are favorable for growing aligned CNT arrays [202].

The catalyst also affects the alignment of CNTs. It is reported that high-quality horizontally aligned SWCNT arrays can be prepared when Cu is used as the catalyst (Figure 32(c)) [203].

2.1.4.2 **Buoyant effect at low gas flow**

When a feeding gas reaches the center region of a quartz tube from the relatively cooler end during CVD growth, a temperature difference between
the substrate surface and the nearby gas will generate a vertical gas density difference (buoyant effect). The buoyant effect of convection flow induced by such gas density gradient can lift the CNTs up above the substrate, and the growth direction of CNTs can then be guided by a shear flow near the substrate surface [204].

When the gas velocity is sufficiently low, the buoyant force will dominate. Figure 33 shows an SEM image of CNT arrays aligned by the buoyant effect. The CNTs are well aligned in parallel arrays. In order to improve the stability of the feed gas, the Reynolds number is decreased to below 1.0 by employing a very low gas flow rate and a narrow CVD quartz tube [204].

2.1.4.3 Trench structure The CNTs can also be oriented by a gas flow without a lift force when the catalysts are deposited on a high platform fabricated on a substrate surface [205,206]. Figure 34(a) shows a microtrench substrate surface structure. Catalytic nanoparticles are deposited on top of the trench. During growth, the nanotubes are freely suspended over the substrate surface and oriented along the flow direction. When CNTs grow long enough, they would touch another microtrench (Figure 34(b)) or settle down to the substrate surface due to gravity.

![Figure 33. SEM image of SWCNT arrays obtained with 0.5 sccm of CH₄ and 1.0 sccm of H₂ at 970°C. Reynolds number is 0.76 during CNT growth. Reprinted with permission from Z. Jin et al., Nano Letters, 7, pp. 2073–2079, 2007 [204]. Copyright (2007) American Chemical Society.](image-url)
The key point of the method is to elevate the catalytic site. The catalysts can be deposited on top of the micotreches fabricated by photolithography [205,206]. A slight tilting of the substrate also raises the catalysts. Long and oriented CNTs grow in the gas flow direction from the substrate edge when a laminar flow dominates the growth dynamics inside the CVD reaction tube [207]. The laminar flow is also important in the growth process. If turbulent flow occurs, the CNTs would grow short and randomly, as observed in the fast-heating method. Depending on the experimental conditions, the flow rate can be 1200 sccm [206], 60–300 sccm [207], or much lower (6 sccm) [204].

In some cases, the catalytic patterns produced by photolithography works similarly and SWCNTs are horizontally aligned between patterns [208]. Compared with other methods, CNTs grown in a gas flow are not only well oriented, but also frequently exceptionally long (in centimeters). So the method has also been used to grow long SWCNTs [202,203].

2.1.4.4 Two-dimensional CNT networks When a multi-step growth is carried out, crossed CNT arrays can be produced using the flow method. Figure 35 shows an SEM image of crossed nanotube arrays grown by a two-step growth process. The CNTs are grown first along one direction under a flow field. Then catalysts are deposited on the substrate and the substrate is rotated 90° to grow another CNT array in a perpendicular direction.

Combined with the epitaxy technique (Section 2.1.5.1–2.1.5.3), 2D crossed CNT arrays can be synthesized by a one-step CVD procedure, as discussed in Section 2.1.5.4.

![Figure 34](image1.png)

Figure 34. A CNT array grown from trench structure. (a) Schematic drawing of nanotube growth from elevated catalyst sites. (b) An SEM image of initial and terminal points of long nanotubes. Scale bar: 50 μm. Reprinted with permission from Z. Yu et al., Chemistry of Materials, 16, pp. 3414–3416, 2004 [206]. Copyright (2004) American Chemical Society.

![Figure 35](image2.png)

Figure 35. An SEM image of a 2D nanotube network grown by multistep growth in a flow field. Reprinted with permission from S. Huang et al., Journal of the American Chemical Society, 125, pp. 5636–5637, 2003 [199]. Copyright (2003) American Chemical Society.
2.1.5. Thermal CVD growth with epitaxy

Epitaxy is another promising approach to align CNTs horizontally. There are three different types of epitaxial growth of CNTs [209]: lattice-directed epitaxy by atomic rows, taking place on atomically flat surfaces; ledge-directed epitaxy by atomic steps, taking place on vicinal surfaces; and graphoepitaxy by nanofacets, taking place on nanostructured surfaces.

2.1.5.1 Lattice-directed growth

The lattice-directed growth of CNTs were observed along the low-index directions of Si (100) [210], Si (111) [210], Au (111) [211], and 6H-SiC (0001) [212,213] surfaces. The synthesized CNTs are usually short. Later, long SWCNTs are aligned in parallel horizontally on R-plane [214–217] and a-plane [217,218] sapphire.

In the lattice-directed growth, sapphire without intentional miscut (less than 0.5°) is usually used as the substrate. SWCNTs grow on atomically flat surfaces. Figure 36(a) shows SWCNTs grown on an R-plane sapphire surface. SWCNTs are aligned in parallel to the [110]-direction. It is believed that the original surface layer of O atoms of the sapphire substrate may be depleted in the CVD process leaving the surface terminated by Al atoms, as shown in Figure 36(b). In this case, [110] becomes the direction of the compact arrangement of Al atoms on the sapphire surface and the arrangement of Al atoms builds the pseudo-one-dimensional arrays, shown as a series of grooves aligned in the direction [110] in Figure 36(b). The CNTs usually grow along the unique 1D array of surface atoms [217,219,220]. It is observed that SWCNTs are aligned along the [100]-direction on (110) a-plane [218,221] or along the [110]-direction on (110) R-plane sapphire [214,215,219]. The preferential growth of SWCNTs along these lattice directions was attributed to higher charge densities along these atomic rows due to electrostatic and van der Waals forces.

Lattice-directed epitaxial growth of SWCNTs also takes place on other atomically flat single-crystal substrates. Recently, for instance, SWCNTs were observed to grow on MgO (001) preferentially along the [110] and [110] directions, and on single-crystal quartz [220,222].

2.1.5.2 Ledge-directed growth

The formation of highly aligned and dense arrays of long SWCNTs was first observed on c-plane sapphires in a CVD process [223]. The c-plane sapphire wafers turned out to have a miscut of a few degrees off the c-plane to produce atomic steps of the vicinal α-Al2O3 (0001) surfaces (Figure 37(a) and (b)). The atomic steps, with a height equal to one-sixth of the hexagonal unit cell \((h = c/6 = 0.219 \text{ nm})\), follow a general direction perpendicular to the miscut direction (Figure 37(b)). Their average spacing is \(d = h/\sin \theta\), where \(\theta\) is the miscut inclination. CNTs grow along the atomic steps of the vicinal α-Al2O3 (0001) surfaces and form highly aligned dense arrays (Figure 37(c)).
In the ledge-directed growth, it is proposed that the higher contact area at the step edge causes the alignment of the CNTs along the edge direction. The uncompensated surface dipoles at the step edges induce electrostatic interactions and enhance the van der Waals force at the step edge, resulting in the alignment of CNTs [223].

Besides $c$-plane sapphire substrates, ledge-directed CNT growth at step edges is also observed on $a$-plane sapphires [218], on $R$-plane sapphires [224,225], and on SiO$_2$/Si wafers [226–228]. Ledge-directed growth of CNTs is also observed on miscut quartz. In this case, the surface consists of vicinal $\alpha$-SiO$_2$ (1101) with steps running along the [2110]-direction [208,229].

2.1.5.3 *Graphoepitaxy* Graphoepitaxy generally refers to the incommensurate orientation of crystals [230] or periodic molecular assemblies [231] by relief features of the substrate, such as nanosteps or nano-grooves, which can be significantly larger than the lattice parameter. Figure 38 shows AFM images of the graphoepitaxial growth of CNTs at nanosteps spontaneously self-assembled on the surface of thermally annealed miscut $c$-plane sapphire [232]. Similar to the
miscut of c-plane sapphire [223], wafers are miscut and mechanically polished to produce atomic steps toward the \([1\overline{1}00]\) or \([1\overline{2}10]\) directions with a height of \(h = \frac{c}{6} = 0.21\) nm (Figure 37(b)). The substrates were then thermally annealed at high temperature. Upon annealing, the thermodynamically unstable atomic steps tend to reduce the surface energy by bunching atomic steps together into faceted nanosteps spaced by flat c-plane terraces. The height of the nanosteps is between one and three times larger than the unit cell, i.e., 1.3–3.8 nm. The atomic steps along \([1\overline{1}20]\) can bunch into stable \(R\)-faceted nanosteps (inset in Figure 38(c)) and the CNTs grow on this surface graphoepitaxially to form CNT arrays along the \([1\overline{1}20]\)-direction (Figure 38(c)).

The atomic steps along \([10\overline{1}0]\) initially bunch into metastable \(P\)-faceted nanosteps (inset in Figure 38(a)), which leads to graphoepitaxial nanotube growth along \([10\overline{1}0]\) (Figure 38(b)). Upon further annealing, the metastable \(P\)-faceted nanosteps break into sawtooth-shaped \(S-/R\)-bifaceted nanosteps (inset in Figure 38(d)) and graphoepitaxy produces nanotubes loosely conformal to alternate \(S\) and \(R\) facets along \([1\overline{1}20]\) and \([2\overline{1}10]\), respectively, as shown in Figure 38(d).

Using artificial nanosteps, SWCNTs can also be horizontally aligned on other substrates. For example, plasma treatment creates some steps with several nanometers height on Si/SiO\(_2\) wafer surfaces. SWCNTs with a site density of 3–8 tubes/μm can be horizontally aligned on such substrate surfaces [226]. SWCNTs can also be directly aligned along the trenches created by electron beam lithography on SiO\(_2\)/Si substrates [227], or along the patterned steps of sapphire [224]. Different from the flow-directed growth where CNTs are grown across the trenches, here the CNTs are grown along the trenches.
2.1.5.4 Two-dimensional CNT networks  Combinations of the CNT epitaxial growth with the field-directed growth (Section 2.1.2) or flow-directed growth (Section 2.1.4) can produce 2D crossbar arrays of CNTs in a one-step CVD procedure.

Figure 39 shows a crossbar array of SWCNTs spontaneously produced in a one-step CVD procedure by simultaneous graphoepitaxy and field-directed growth, perpendicular to each other. The miscut c-plane sapphire is annealed to produce the nanosteps along the [11\220]-direction, while an electric field is applied perpendicularly to the nanosteps. The nanotubes originating from catalyst nanoparticles lying on the sapphire grow along the faceted nanosteps, while the nanotubes emerging from the catalyst on patterned amorphous SiO2 stripes grow freely without interacting with the surface, in a way that allows their alignment by the electric field, eventually falling across the nanotubes previously grown on the sapphire. SWCNTs grow along the atomic steps of miscut c-plane sapphire surfaces [223], or along the 1.3–4 nm high-faceted nanosteps of annealed miscut c-pane sapphire [232]. The alignment of the graphoepitaxial SWCNTs is unaffected by external forces, such as electric field and gas flow field [223,232]. So the nanotubes originating from the catalyst nanoparticles lying on the bare sapphire grow along the nanosteps, while the nanotubes originating from catalyst nanoparticles lying on the amorphous SiO2 islands grow up freely and are aligned by the electric field perpendicular to the nanosteps. The two alignment mechanisms take place selectively on miscut c-plane sapphire and patterned amorphous SiO2 strips, respectively, without mutual interference, producing dense nanotube grids.

Similar to the combination of lattice-directed growth and electric field-directed growth, 2D crossbar structured CNTs can also be produced in a one-step CVD process from a combination of lattice-directed growth and flow-directed growth [233]. Figure 40 shows the mechanism and SEM images of SWCNT crossbar structures grown on quartz substrates in this way. The average length of lattice-orientated SWCNTs can reach hundreds of microns, and the spacing between the nanotubes is about several microns. Gas flow-directed SWCNTs are millimeters long and the spacing between nanotubes can be reduced to about 10 \( \mu \text{m} \). The CNT node density of the crossbar structure is about \( 10^7 \text{ cm}^{-2} \).

Combining lattice-directed growth and graphoepitaxial growth, bent CNTs can be horizontally grown on crystal substrates, like R-plane sapphire with artificial nanosteps [224]. SWCNTs first grow along the specific crystallographic [\11\0\1\]-direction on R-plane sapphire due to the lattice-oriented growth and then grow along artificial nanosteps, perpendicular to the first SWCNT.

growth direction $[1\bar{1}0\bar{1}]$. These nanosteps change the nanotube growth direction from $[1\bar{1}0\bar{1}]$ to the nanostep direction with the bending angle of nearly $90^\circ$.

2.1.6. Thermal CVD under magnetic fields

Another approach to align CNTs is to control the orientation of catalyst nanoparticles [234,235]. Ferromagnetic materials, such as iron, nickel, and cobalt, have been used for CNT catalysts and have one crystallographic magnetic easy axis. The magnetic easy axis tends to be parallel to the magnetic field. As a result, an applied magnetic force can orient these magnetic catalytic nanoparticles, like catalytic iron nanoparticles [234] and Fe$_3$O$_4$ nanoparticles [235]. Because only a certain nanocrystalline facet of catalytic nanoparticles is catalytically active and the diffusion rate of carbon atoms on the facet is the highest (such as (220) of Ni) [165,236], the CNTs preferentially grow from the certain facet of the catalytic nanoparticles and the grown CNTs are oriented at a certain angle. Figure 41 shows the histogram distribution of CNTs synthesized with or without an external magnetic field. When a magnetic field is applied during the CNT growth, CNT grow preferentially along two certain directions.

2.2. Ex situ techniques for CNT alignment

Ex situ assembly of CNTs is a post-synthesis method for CNT alignment. CNTs are first synthesized by CVD or other methods, and then are assembled by electric fields, magnetic fields, force fields, or other methods. Compared with the in situ techniques, the ex situ techniques are free of collateral growth restrictions such as substrate material and growth temperature.

2.2.1. Electric fields

CNTs can be aligned under electric fields in liquids [237–240]. The electric fields can be DC or AC fields. Figure 42 shows SEM images of aligned CNTs between two electrodes. Gold interdigitated electrodes are fabricated by vacuum deposition on Si/SiO$_2$ substrates. Then the substrates are immersed in the SWCNT suspension and an electric field is generated between the electrodes [237]. The CNTs are polarized in the suspension by the electric field because of dielectric mismatch between CNTs and the liquid. The polarization moment rotates the CNTs toward the direction of electric field lines, therefore aligning them in a common direction. After being aligned, the CNTs are taken out with the substrates and dried in air.
Another approach to align random CNTs, also related to electric-field-directed alignment, is the orientationally selective ablation of random networks with a planarly polarized laser [241]. SWCNTs oriented with a projection in the plane of polarization were selectively ablated, leaving on the surface only those that are oriented perpendicular to the plane of polarization.

2.2.2. Magnetic fields
Calculations reveal that CNTs exhibit diamagnetic or paramagnetic responses depending on the magnetic field direction, the helicity of CNTs, the Fermi energy of CNTs, and the radius [101]. Metallic SWCNTs are paramagnetic in the direction of their long axes, confirmed by experimental
Figure 43. (a) Field dependence of the magnetic moment of CNTs at high fields. The CNTs with diameter of 2–10 nm are grown by arc-discharge technique. (b) Experimental setup to align CNTs in magnetic fields. (c) Small-angle neutron scattering pattern of CNTs aligned in magnetic fields shown in (b).


data (Figure 43(a)). Under magnetic field $B$, the CNTs with magnetic dipole moment $P$ receive a torque vector given by $\tau = P \times B$. At high magnetic fields, the magnetic force applied on the CNTs can align the whole CNTs along the magnetic field direction.

Usually CNTs are dispersed ultrasonically in a liquid epoxy resin and then the mixture is left in a magnetic field at room temperature before it is cured (Figure 43(b)). The alignment of CNTs in the liquid under a magnetic field occurs due to the cooperative effect of the magnetic torque exerted by the magnetic field directly on the nanotubes and the hydrodynamic torque and viscous shear (i.e., drag forces) exerted on the nanotubes by the polymer chains [244–248]. Small-angle neutron scattering of CNTs indicates that the CNTs really rotate and align in the magnetic field (Figure 43(c)). The calculation of SWCNT susceptibilities predicts that a field in the order of 10 T can produce an observable alignment in a liquid suspension of SWCNTs [249]. Transmitted light measurement indicates that 90% of purified SWCNTs can be aligned in dimethylformamide along a magnetic field (19 T) axis with a CNT axial orientation within $17 \pm 1^\circ$ [250]. The alignment
energy from CNT susceptibility should be much higher (> $5\kappa_B T$) to overcome the Brownian motion with an average energy of $\kappa_B T$, where $T$ is the experimental temperature. Additionally, X-ray diffraction experiments also confirm that CNTs can align along the magnetic field direction.

The as-synthesized CNTs are usually paramagnetic because of the entrapped catalytic nanoparticles in the CNTs [242,244]. The magnitude of magnetization of the as-synthesized CNTs is typically several orders of magnitude higher than the purified CNTs. Under a magnetic field, the as-synthesized CNTs also tend to align parallel to the external magnetic field. In order to increase the susceptibility of individual CNTs, they may be coated or filled with magnetic nanoparticles [251].

2.2.3. Mechanical methods

CNTs can be effectively aligned by various mechanical methods. Below we briefly review these mechanical methods.

2.2.3.1 Stretching method

Stretching method is probably the simplest ex situ method to align CNTs. CNTs are aligned under an external force field.

Figure 44 shows a simple stretching method to align CNTs on substrates. The CNTs are synthesized first on a substrate. The as-synthesized CNTs are random, tangled, and curved (Figure 44(a)). Once the substrate is broken in the middle, a force pulls the CNTs on the substrate and the CNTs are aligned (Figure 44(b)). The aligned CNTs are parallel to each other and perpendicular to the crack.

CNTs are also aligned in polymers. The CNTs are first embedded in a polymer matrix, and aligned CNTs can be obtained by cutting thin slices of the CNT/polymer composites [253]. The CNT composites are also casted into films and then cut into small strips. Mechanically stretching the cast strips to a desired stretching ratio at high temperature aligns CNTs parallel to the stretching direction [254]. 2D X-ray diffraction patterns indicate that the CNTs are aligned with their longitudinal axes parallel to the stretching direction. The mechanical stretching method has been used to align SWCNTs in polymeric composite films [255,256].

Different from the force field produced by stretching, spinning produces a radial force field. When CNTs are dispersed in thermoplastic resins and melt-spun at high temperature, they can be well aligned in the composite along the spinning direction [257].

Figure 44. (a) Thermal CVD-grown MWCNTs deposited on the substrate. The grown CNTs are curled and randomly distributed on substrate surface. (b) Aligned DWCNTs after being pulled out. The CNTs are straight and parallel to the substrate surface. Reprinted from Chemical Physics Letters, 368, W.Z. Li et al., pp. 299–306 [252]. Copyright (2003), with permission from Elsevier.
The stretching method can macroscopically align the CNTs while not providing deterministic control over individual CNT alignment or position during assembly. The direction of CNTs cannot be aligned along the force field perfectly.

2.2.3.2 Spinning methods The spinning method has been successfully used to fabricate CNT ropes and CNT clothes [258–263]. Figure 45 shows a CNT sheet assembled by a spinning method. The CNTs are well aligned along the force direction. The transparent thin CNT sheets are fabricated in meters. This kind of nanosheets can be used for TEM grids (Section 5.1.2), incandescent displays and lighting (Section 4.1.4), thermoacoustic loudspeakers (Section 5.3), etc.

Up to now, two main kinds of spinning methods, wet-spinning and dry-spinning, have been invented. In a wet-spinning process, the synthesized CNTs are dispersed in a melt or a liquid/solution, aligned by flow processing, and then converted into a fiber through cooling or solvent removal [265]. The dry-spinning method directly spins the CNT forests synthesized by CVD [93], directly spins a CNT aerogel formed in the reaction zone [262], or spins cotton-like raw CNTs to form CNT yarns or continuous fibers. Here we do not review these spinning methods.
in detail since there are already some thorough reviews on wet-spinning from solution [209,266], on dry-spinning [209,259], and on electrospinning from CNT composites [258].

2.2.4. **Other ex situ methods**

Besides the *ex situ* methods discussed above, CNTs can also be aligned by fluidic methods [97], electrophoresis [267,268], surface forces [269], surface acoustic waves [270], and by chemically directed assembly [271].

2. **Direct-current PECVD**

Probably the most widely used growth method for aligned CNTs is DC-PECVD due to its effectiveness in alignment control and equipment setup simplicity. It is, therefore, worth to dedicate this section to review this technique in more thorough details while also not limiting the discussion to a single type of electrical discharge (plasma). Besides, comprehensive reviews on various aspects of PECVD techniques for aligned CNT growth is already available [272,273]. Although it has been reported that, in DC configurations, CNTs can be grown under either a positive or negative bias [274], the most popular choice is applying a negative bias on the substrate probably to utilize the ion bombardment effects that will be discussed in the following paragraphs. Unlike in the cases of AC plasmas where identical parallel plate electrodes are predominantly used for growth uniformity, DC plasmas require a higher breakdown voltage to initiate and therefore the electrode shapes need to be modified to facilitate the initiation. The simplest and most popular option is to have the positive electrode of a much smaller effective surface area, e.g., a small plate or even a rod end with a flat or pointy tip, so that its local sharp edges can more easily induce strong local electric fields to initiate the plasma. Besides, this configuration can also provide relatively uniform CNT growth over centimeter scales, sufficient for laboratory research. There are also specific characteristics of DC plasma growth such as the substrate conductivity requirement and dark discharge plasma states, which will be demonstrated together with some general growth aspects in all PECVD processes.

3. **Equipment setup and growth procedure**

An exemplary schematic setup of the DC-PECVD apparatus is illustrated in Figure 46 [275]. Inside a vacuum chamber (1), a rod-shaped molybdenum anode (2) hangs vertically about 1–2 cm over...
a horizontal molybdenum cathode plate (3) which also serves as a sample stage. The diameters of the rod and the plate are 0.25” and 4”, respectively. Underneath the cathode plate is a resistive plate heater (4) powered by an external AC voltage (5). The two electrodes are connected to an external power supply (6), MDX-1K Magnetron Drive (The Advanced Energy®), which runs on a constant voltage, current or power mode. Feedstock gases are introduced into the chamber via a single gas pipe (7) after going through respective flow controllers (8, 9), and the chamber evacuation is solely executed by a mechanical pump (10). The evacuation speed and therefore the system pressure are manually controlled by a gate valve (11) which throttles the evacuation channel. In addition to the basic structure in Figure 46, a pressure sensor is installed in the chamber base plate, and a thermocouple is first insulated in a thin quartz tubing and then brought into contact to the cathode for temperature monitoring. Compared to the other plasma sources which are mostly AC, the major setup difference is that the anode surface is shrunk into a much smaller size than the cathode. This makes the sharp edges of the anode to be almost the closest geometrical point to the cathode where the plasma should initiate and the edges allow a relatively low breakdown voltage due to local field enhancement.

The DC-PECVD process for vertically aligned CNT arrays includes four basic steps, namely evacuation, heating, plasma generation, and cooling. A typical procedure can be described as follows. After samples are loaded onto the sample stage, the chamber is evacuated to a base pressure of around $10^{-2}$ Torr. NH$_3$ is then introduced into the chamber to reach a pressure of 8 Torr and the heater is turned on to gradually elevate the stage temperature. Typical growth temperatures used are in the range of 450–600°C which can be normally reached in a period of 15–30 min. The pressure is maintained by adjusting the aperture of the gate valve. As soon as the temperature and pressure are stabilized, a DC bias voltage of 450–650 V is applied to the gap between the two electrodes to ignite an electrical discharge (plasma) over the sample. The plasma current intensity may typically vary within 0.1–0.5 A. C$_2$H$_2$ is then introduced to trigger the CNT growth. The flow rate ratio of NH$_3$:C$_2$H$_2$ is usually around 4:1 which results in a minimum amount of amorphous carbon formation. And the growth time may vary from a couple of minutes to hours depending on the growth rate and desired CNT length. When the end of growth time is reached, the bias voltage is removed immediately to terminate the plasma. Meanwhile, the gases are discontinued and the gate valve is fully opened to evacuate the chamber. The heater is also turned off for the samples to cool down naturally. Inert gases such as N$_2$ or Ar can also be fed into the chamber to speed up the cooling process if desired.

Again, the above setup and procedure should be taken as a basic example with room for variations in peripheral aspects such as triode-type electrode setups [274], different mechanisms for substrate heating, and application of other reacting gases such as CH$_4$ and H$_2$. The apparatus and process simplicity has greatly facilitated the adoption of this technique by many research groups around the globe and has helped to push the aligned CNT research forward rapidly and significantly.

3.2. Substrate and underlayer

For any growth process of CNTs, the general requirements for the underlying substrate (or underlayer coated onto the substrate) are that (1) it has to be both physically and chemically stable for up to the growth temperature and (2) its surface must not poison the catalyst particles in contact (such as by forming an inactive alloy) which can be frequently avoided by an inert buffer layer coating. For PECVD processes, the substrate must also be chemically stable under the plasma which is rich of H-species. Some weakly bonded oxides such as indium oxide can be quickly reduced in this plasma and is therefore usually not applicable as the substrate or underlayer. And for DC-PECVD, in particular, the substrate must be electrically conductive to sustain a continuous
DC current flow through its surface where the CNTs grow from. Most metals and semiconductors (such as silicon wafers) are very good substrate materials, and insulating substrates such as glass [32] and polyimide [276] can be first coated with a conductive layer to work properly (requiring electrical contact of the conductive layer to the cathode during growth). Although it has been reported [32] that directly depositing catalyst films onto glass may still result in aligned CNT growth, this phenomenon should be due to the formation of a conductive amorphous carbon layer which connects the narrow spacing among the dewetted catalyst particles, which is more directly observed on polyimide substrates [276]. Indeed, large-spacing catalyst particles are found to always require a conductive substrate or underlayer for CNT alignment. Common transparent conductive oxide (TCO) thin films can also be applied as conductive underlayers on insulating glass substrates for aligned CNT growth by DC-PECVD, although it requires proper choice of the discharge conditions [276], which will be discussed in detail later.

3.3. Growth temperature

One of the major advantages of using PECVD growth techniques is the low growth temperature. The ionization of the neutral hydrocarbon molecules inside the plasma facilitates the breaking of the C–H bonds and lowers the activation energy of the CNT growth. Indeed, the activation energy for PECVD processes is experimentally measured to be $\sim$0.3 eV, much lower than the $\sim$1.2 eV for thermal CVD processes [277]. Figure 47 shows the extrapolated activation energy values for DC-PECVD and thermal CVD growth based on experimental data. DC-PECVD growth temperature has successfully been demonstrated to be as low as 390°C for bamboo-like CNTs and 120°C for amorphous CNFs [278], compared to CVD growth temperatures in the 500–700°C range.

Although at very low temperatures the C-atoms in the grown structure begin to be more disordered (Figure 48), the fact that C-atoms can still diffuse and precipitate along the catalyst surfaces to result in nanostructure growth demonstrates that carbon diffusivity is just the limiting

Figure 47. Arrhenius plots for CNT growth rates on different catalysts in NH$_3$ diluted C$_2$H$_2$. Reprinted figure with permission from S. Hofmann et al., Physical Review Letters 95, pp. 036101-036104, 2005 [277]. Copyright (2005) by the American Physical Society.
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Figure 48. CNF PECVD deposited at (a, d) 500°C, (b, e) 270°C, and (c, f) 120°C. (a)–(c) SEM images of CNF arrays and (d)–(f) HRTEM images of a CNF. Reprinted with permission from S. Hofmann et al., Applied Physics Letters, 83, pp. 135–137, 2003 [278]. Copyright (2003), American Institute of Physics.

factor for low-temperature growth rate, whereas the feedstock hydrocarbon dissociation is really the bottleneck process for growth initiation. This understanding leads to remote-plasma CVD processes for growth temperature lowering [206,279], which is beyond the scope of this review. Since alignment can still be achieved at these low temperatures (Figure 48), many application opportunities open up, especially in templating on plastic substrates where temperature is sensitive and morphology is more essential than crystallinity.

3.4. Plasma heating and etching effects

Although the primary intention to introduce plasma in CNT growth is to reduce the activation energy by facilitating hydrocarbon dissociation as stated above, the plasma has two other major collateral effects which must be taken into consideration and sometimes utilization: heating and etching. As a DC voltage higher than the breakdown threshold on the Paschen curve is applied across the electrodes, free electrons are energized and subsequently ionize neutral species through elastic collisions, generating more free electrons. Such an avalanche process causes an electrical discharge state of a collection of free electrons, ions, and neutral species, which is called plasma. The collisions among energized charged particles and neutral molecules inside the plasma body raise the gas temperature which can be conducted to the substrate. Also the ionic bombardment onto the substrate surface (sitting at a negative potential on the cathode) caused by positive ions accelerated across the plasma sheath field incurs ohmic heating of the substrate. Both processes together can lead to significant substrate heating to above 700°C in real growth chambers without a separate heater [172]. Figure 49 shows that plasma heating can raise the substrate temperature as much as using a separate heater. Aligned CNTs can grow with such plasma heating just as well as with separate heating mechanisms. It is also this plasma heating effect that puts the accuracy of many low-temperature PECVD growth results into question. Special care has to be taken during the
experimental setup to measure the substrate temperature which includes the heating contribution from the plasma.

Besides partially causing the plasma heating effect, the ion bombardment on the substrate surface exposed to the plasma also causes physical or chemical mass removal, especially at locations where the local field strength is high. Such a plasma etching effect is widely conceived to account for the removal of amorphous carbon during CNT growth and facilitate the catalyst thin-film dewetting prior to CNT growth. One of the clearest demonstrations of the plasma etching effect is done using 2D periodic catalyst particle arrays where particle size (and the resulting CNT diameter) is shown to decrease with increasing time of plasma exposure before CNT growth [177,280]. This provides an opportunity to tailor the catalyst particle size and control the resulting CNT diameter by exposing the particles to a certain period of plasma etching prior to CNT growth. Besides reducing the particle size, the plasma etching also rounds off any sharp edges of the original particle shape and, in some cases, facilitates and modifies the breaking down (dewetting) of a continuous film [276,281–283].

3.5. Plasma states

For DC plasmas, there exists a series of discharge states with different current density levels. From current density levels of low to high, a DC plasma can experience dark discharge, glow discharge,
and arc-discharge states [284]. Since right after gas breakdown, the plasma directly enters the glow discharge state which is most frequently used for most PECVD growth processes. If the current density of a glow discharge state is continuously lowered crossing a critical point when the bias voltage experiences an abrupt increase, the plasma enters a new state of dark discharge. The extremely low current density level of dark discharges can significantly reduce the plasma heating and etching effects, which may be beneficial to aligned CNT growth in many scenarios where such effects are detrimental. For instance, aligned CNF arrays with exceptionally small diameters (<10 nm) are successfully grown using a dark discharge plasma (Figure 50), and the process also allowed direct CNF growth on TCO underlayers such as ITO and ZnO at a moderately low temperature [276]. Counterintuitively, dark discharges have a highly uniform nature which is suitable for large-scale applications.

3.6. Catalyst crystal orientation

It is almost always preferable to have identical CNTs or CNFs in an aligned array over a macroscopic distance. Further work needs to be done to improve the uniformity across an array by starting from catalyst particles of identical morphology and crystallographic orientation. It has been shown that during CNT growth by DC-PECVD, the crystallographic orientations of the catalyst particles are preserved [285]. Figure 51 shows the XRD results comparison among the original Ni film, the dewetted Ni particles, and the Ni particles embedded in the CNTs after growth. Such preservation means that it is useful to prepare catalyst particles all with the same crystallographic orientation by epitaxial growth methods [286,287] or graphoepitaxy [288–290], etc. The motivations for such epitaxial control of the catalyst particles are: (1) carbon diffusion rates along different catalyst crystal planes are different, meaning that catalyst particles with the same orientation might provide the same CNT growth rate [285,291]; (2) CNT cap formation is determined by the surface facets of the catalyst particles, meaning that catalyst particles with the same orientation might yield CNTs with the same atomic structure (chirality, diameter, etc.) [292–294]. Of course, precise control of CNT structures on the atomic level in an aligned array will involve much more than controlling the crystallographic orientation of the catalyst particles, but this is certainly a first and necessary step to take. And the orientation preservation of the catalyst particles during the DC-PECVD process provides the prerequisite condition for achieving this ambitious goal.
3.7. Electric field manipulation

Since CNTs grow along the electric field lines in the DC-PECVD process, one can impose special conditions where CNTs grow at an angle to the substrate plane. This is usually done at a relatively small scale by modifying the local field direction using a second conductor block during the PECVD growth in the chamber, such as that shown in Figure 52(a). Furthermore, once the first...
inclined CNT growth is completed, the setup can be changed to result in a different field direction and then the growth can be restarted by re-activating the catalyst particles [295] or introducing new catalysts [296]. Repeating the above procedure may result in zigzag-shaped bent CNT arrays (Figure 52(d)), which exemplifies the degree of alignment manipulation using variations of conventional DC-PECVD methods. Such techniques are valuable for the study of catalytic properties of nanoparticles and the electric field effects on CNT growth and, most importantly, widen the possibilities to achieve more complicated and well-controlled CNT morphologies. One can imagine that in an advanced PECVD setup where the substrate is surrounded by various conductors whose positions and shapes can be remotely controlled at all time during the growth by an external controller, CNTs can be accurately grown into almost arbitrary shapes with even more variety and complexity in a quite straightforward way.

4. Properties and applications of aligned CNT arrays

Individual CNTs have wide applications because of their unique properties, such as nanoprobes in scanning probe microscopes [297], tips of atomic force microscopes [298,299], electron field emitters [300], mechanical memory elements [301,302], SWCNT chemical sensors [303], quantum resistors of MWCNTs [304], nanobalances to weigh nanoparticles [305], nanodevices [306], transistors [65,307,308], logic gates of SWCNTs [309], MWCNT nano-motors without friction (molecular linear motors and rotational motors [310]), nano-electronics [311,312], nano-test tubes [313], molecular delivery to shuttle macromolecules into cells [314–316] or rapid transport of gold nanoparticles across the cell wall [316], high-pressure nano-cylinders [317], etc. However, it is not the emphasis of this review to discuss applications of individual CNTs. We refer the interested readers to the relevant reviews on this topic [146,302,318] for detailed information.

Bulk CNT ensembles without ordering are also widely applied in many cases to improve the mechanical, thermal, electrical, and other physical properties of the target materials. For example, bulk CNTs have already been used as composite fibers/reinforcing additives in polymers or ceramics to improve the mechanical, thermal, and electrical properties of the bulk products, such as ceramic composites [319–328] and metal composites [319,323,324,326,329–331]. In a fully dense SWCNTs/Al2O3 composite without damaging the CNTs, a fracture toughness of 9.7 MPa m1/2, nearly three times higher than that of pure nanocrystalline alumina, was achieved in the spark plasma-sintered composites [332] and in hot-pressed samples [327,330]. CNTs have high thermal conductivity and have therefore been used as additives to increase the thermal conductivities in liquids [333]. Random CNT bulks are also used for solar cells [334,335], fuel cells [336,337], and hydrogen storage [338,339]. The readers are referred to the respective literatures [331,340–356]. The research on the application of CNT bulks is a rich field that has already been discussed in several excellent reviews.

Aligned CNT arrays have unique properties from random CNT bulks and have wider application potentials, including field emission and flat screens, ultracapacitors, nanoelectrode arrays, fuel cells, solar cells, transistors, chemical and biological sensors, due to the ordering of their structures. In the following sections, we focus on the applications of the well-aligned CNT arrays and talk about these applications in details.

4.1. Field-emission devices

Field emission in solids occurs in intense electric fields (the gradients are typically higher than 1000 V/μm for pure metals) and is strongly dependent on the work function of the emitting material. In a parallel-plate arrangement, the macroscopic field \( E_{\text{macro}} \) between the plates is given by \( E_{\text{macro}} = V/d \), where \( d \) is the plate separation and \( V \) the applied voltage. If a sharp object is
created on a plate, then the local field $E_{\text{local}}$ at its apex is greater than $E_{\text{macro}}$ and can be related to $E_{\text{macro}}$ by

$$E_{\text{local}} = \gamma \times E_{\text{macro}}.$$  \hfill (1)

The parameter $\gamma$ is called the field-enhancement factor and basically determined by the shape of the object. Because the field-emission characteristics are determined by the local field $E_{\text{local}}$, the higher the $\gamma$-value of the object, the lower the value of $E_{\text{macro}}$ at which significant emission occurs.

CNTs have high aspect ratios (length divided by diameter) and induce very high local electric field intensities around the tips. So CNTs are considered as one of the best electron-emitting materials. Emission of CNTs was first reported in 1994 [357] and several papers were published in the subsequent three years [300,358–370]. From 1998, interests in field-emission properties of CNTs undertook a very sharp increase all over the world and thousands of papers have been published ever since, such as field-emission property of aligned CNT arrays [36], due mainly to the successes in the alignment of CNTs. The early history of CNT field emission is reviewed recently [371].

The intrinsic field-enhancement factor $\gamma$ of an individual CNT in the planar diode configuration can be approximated by [372]

$$\gamma_0 = 1.2 \times \left(2.5 + \frac{l}{r}\right)^{0.9},$$  \hfill (2)

where $l$ and $r$ are the length and the radius of the CNT, respectively.

Typical field-enhancement factors ranging from 30,000 to 50,000 can be obtained from individual CNTs. The field-enhancement factors of CNT films consisting of random CNTs are much smaller than those of individual CNTs because of the planar substrate supporting the CNT film. $\gamma$ from 1000 to 3000 can be usually obtained from the CNT films [373]. A high field-enhancement factor of $1.88 \times 10^4$ was achieved for CNTs grown on carbon cloth [367]. A recorded low turn-on electric field of less than 0.4 V/μm is required to reach an emission current density of 1 mA/cm$^2$ [367]. The field emission of the CNT films consisting of random CNTs has been widely reviewed recently. Next we talk about the field emission of aligned CNTs and their applications.

4.1.1. Field emission of aligned CNT arrays

The field-enhancement factor $\gamma$ of CNT arrays can be experimentally determined from the slope of Fowler–Nordheim plot if the work function is known. The extracted field-enhancement factor $\gamma$ from the Fowler–Nordheim plot is affected by the adsorbates [374] and by the geometry of configuration [375].

The Fowler–Nordheim dependence of an aligned CNT array takes the form [371]

$$j \approx 1.56 \times 10^{-6} \frac{(\gamma E_{\text{macro}})^2}{\phi} \exp\left(-\frac{0.683 \times 10^7 \phi^{3/2}}{\gamma E_{\text{macro}}} \right),$$  \hfill (3)

where $j$ is the current density (in A/cm$^2$), $\phi$ the work function (in eV; it is assumed that $\phi = 4.7$ eV for CNT nanotubes), and $E_{\text{macro}}$ the average electric field (in V/μm). In the Fowler–Nordheim coordinates of MWCNTs, $\ln[j/(E_{\text{macro}})^2] \propto 1/\gamma E_{\text{macro}}$. The field-enhancement factor $\gamma$ is experimentally determined from the slope of the Fowler–Nordheim plot.

In the typical measurements of Fowler–Nordheim plots, the field-emission currents of CNT arrays are measured in a simple diode configuration. The anode is a molybdenum disk with a diameter of 5 mm and the substrate on which the CNT arrays have grown works as a cathode.
Figure 53. (a) The measured current densities as a function of the macroscopic electric field for eight samples. (b) SEM micrograph at a grazing incidence of 45° to the substrate of the four samples. The white scale bar corresponds to 10 μm. (c) Length and areal density of eight CNT arrays. Reprinted with permission from S.H. Jo et al., Applied Physics Letters, 82, pp. 3520–3522, 2003 [186]. Copyright (2003), American Institute of Physics.

The gap between the silicon substrate and the anode is 300 μm [186]. Figure 53 shows the field-emission current of CNT arrays measured by the diode method.

Figure 53 clearly shows that the field enhancement of CNT ensembles is affected by the length of CNTs and the spacing between them. So it is important to characterize the effects of length and spacing on field-emission properties in order to obtain a large and uniform field-emission current at low electric field. The studies on the effects of length and spacing have been reported for vertically aligned CNT arrays [186,359,361,376–378] as well as for randomly oriented CNT ensembles [190,379,380].

The field-enhancement factors of dense CNT arrays are smaller than those of CNTs with lower site density because the electric field on one nanotube is screened by the proximity of neighboring nanotubes. Through analyzing the vertically aligned MWCNT arrays, it is found that, for a given length of CNTs, γ increases as the spacing of CNTs is increased [186]. It is estimated that γ is nearly saturated when the site density is about $10^6$ cm$^{-2}$ and the length is longer than 10 μm. However, for the very-high-density CNT assemblies, the increase in length increases γ slightly, whereas for the very short CNT arrays, the increase in spacing does not effectively reduce γ. It is found that the field emission was critically affected by the CNT height that protruded from the surface because of the field-screening effect [376].
The theoretical simulation indicates that the field emission is optimal when the nanotube height is close to the inter-nanotube distance (Figure 54). The theory predicts that the field emission is best enhanced when the CNT spacing is one-half of the height [190].

Taking into consideration the effect of spacing between CNTs, the field-enhancement factor $\gamma$ of CNT arrays can be approximated by [373]

$$\gamma = \gamma_0 \left[ 1 - e^{-2.3172 \times \frac{R}{l}} \right]$$

where $R$ is the spacing between CNTs and $l$ the height of CNTs.

The emission property of aligned CNT arrays is not satisfactory if the areal density is higher than $10^9 \text{ cm}^{-2}$ because of small enhancement factors at the CNT tips [189]. An areal density of about $10^7 \text{ cm}^{-2}$ has been estimated to be the optimal density for electron emission properties in terms of both emission site distribution and current density [190]. PECVD discussed in Section 2.1.3 provides a valuable approach for obtaining optimal emitter density of CNTs. The CNT forests grown by the thermal CVD method under crowding effect (see Section 2.1.1) is not good for field emission because of high site density.

To enhance the field-emission properties of aligned CNT arrays, some effective methods have been carried out, such as plasma treatments in $\text{H}_2$ [381], in $\text{O}_2$ [382] after growth, controlling the site densities of CNTs during growth to decrease the electrostatic screening effect [178], laser treatment [383], annealing in oxygen or ozone to open the end of the CNTs [384], and thermal oxidation in air [369]. The field-emission current density can be significantly improved by a factor of 4 [369] or even 8 [384] after the treatments.

More detailed information on the physics of electron emission of CNT arrays can be found in the recent published reviews [385–388].
When a bias potential is applied between a CNT-coated surface and an anode, a strong local field is produced at the small CNT tips, inducing electrons to tunnel from the tips into the vacuum space toward the anode. When a phosphor layer is coated on the anode, the field-emitted electrons will bombard the phosphor to produce light, a useful process in flat-panel displays/lighting sources. Prototype devices using the superior field-emission properties of aligned CNT arrays have been demonstrated, including X-ray sources, flat-panel displays, and lamps. We will introduce some applications of vertically aligned CNT arrays in the following sections based on their field-emission properties.

4.1.2. CNT array emitters

Based on the emission properties of aligned CNT arrays, CNT field emitters are produced [190, 389,390]. At present, CNT emitters operate stably under moderate-vacuum conditions ($10^{-8}$ Torr), which is an advantage over metal field emitters such as those made of tungsten and molybdenum requiring ultra-high vacuum environments ($10^{-10}$ Torr) [391].

The short-term emission of CNT emitters is stable with a current density of 1 mA/cm$^2$ and a fluctuation of 2% without bias resistors. This kind of emission current is sufficient for practical applications in flat-panel displays.

4.1.3. High-intensity electron sources

Based on their field-emission properties, aligned CNT arrays can be used as high-intensity electron guns [359]. Such electron sources are air-stable and longtime reliable with field-emission current densities of $\sim 0.1$ mA/cm$^2$ under an applied voltage as low as 200 V. Current densities greater than 100 mA/cm$^2$ have also been realized under 700 V, making such electron sources suitable for high-intensity applications.

In addition to the emission current density, the stabilities of aligned CNT arrays (the variation of emission current over time) are also critical to obtain a long-lasting reliable field-emission electron source. The field-emission current from CNTs usually shows an unstable behavior in air due to reaction with ambient gas. When the CNTs are coated by amorphous layers, the coated CNTs have stable emission current for more than 60 h in vacuum (Figure 55), while the emission current of non-coated CNTs decreases with time [367]. The emission current of coated CNT arrays is decreased after an air exposure but recovers after re-evacuation.

4.1.4. Lighting

Three kinds of CNT lighting devices have been demonstrated. One is the cathodoluminescent light-emitting element of cylindrical geometry [392,393] (Figure 56). MWCNTs are grown on a conductive cathode of radius $r_1$, located on the symmetry axis of the cylindrical anode of inner radius $r_2$. The anode is a glass tube with a conductive coating and a phosphor layer on the inner surface. When working at an operating voltage of 5.4 kV, the emitted current density is 0.5 mA/cm$^2$ on the cathode and 0.06 mA/cm$^2$ on the anode [392]. The emitted light intensity amounts to 10,000 cd/m$^2$, comparable to a commercial fluorescent tube (11,000 cd/m$^2$).

The second kind (Figure 57) is the diode-structured flat-panel luminescent light source with a CNT array field-emission cathode [391,394]. In such a flat-panel source, the CNT arrays as the cathode are vertically grown on a substrate with patterned catalyst particles (Figure 57(c)). Under high voltages, the electrons from CNT tips bombard onto a phosphor screen to generate light, similar to the first kind of light source.

The underlying substrates also affect the field-emission properties of CNT emitters. Figure 58 shows the typical current density versus the electric field intensity for CNT emitters on stainless
Figure 55. (a) Stability of field-emission current with time in vacuum. The CNT arrays are covered with an amorphous layer of 10–25 nm thickness. (b) An SEM image of the CNT arrays. The average length and site density of CNTs are 8.5 μm and $1 \times 10^6$ cm$^{-2}$, respectively. The diameter of the CNTs is in the range of 50–80 nm. Reprinted with permission from S.H. Jo et al., Applied Physics Letters, 84, pp. 413–415, 2004 [367]. Copyright (2004), American Institute of Physics.

Figure 56. Luminescent field-emission device in cylindrical geometry. (a) Schematic structure of the device. (b) Product of the CNT field-emission device. Reprinted with permission from J.-M. Bonard et al., Applied Physics Letters, 78, pp. 2775–2777, 2001 [392]. Copyright (2001), American Institute of Physics.

Steel substrates and on nickel substrates, at $1 \times 10^{-6}$ Pa and room temperature [394]. The inset in Figure 58 shows Fowler–Nordheim (F–N) plots of the same emission data. CNTs on stainless steel ($3 \times 3$ mm$^2$) begin to emit electrons at a lower electric field level than CNTs on nickel, indicating that the emission property of CNTs depends also on the substrate material supporting the catalysts for CNT growth. The emission current density of the stainless steel substrate displays an onset field near 1.2 V/μm. A field-emission current density of 1 mA/cm$^2$, the critical value required for conventional flat-panel displays, is achieved at a field intensity level of about 3 V/μm. Strong saturations above 1 mA/cm$^2$ on nickel substrates and 100 mA/cm$^2$ on stainless steel substrates are observed, with the F–N slope diminishing by a factor of 2 on nickel substrates and by a factor of 3 on stainless steel substrates. These current saturations for aligned CNT emitters are also reported in random CNT emitters [395,396].

CNT-based lighting sources can emit white light as well as colored light. The CNT lighting sources can provide stable emission, long lifetimes (over 4000 h), and low emission threshold voltages [388,391]. The emission current of a white-color CNT device is stable with a fluctuation of 2% without bias resistors. The lifetime of such device exceeds 10,000 h recently [394]. The luminance of about $6 \times 10^4$ cd/m$^2$ for green light is obtained using CNT cold cathodes [391].
Ultrahigh luminance light sources can be produced by employing special MWCNTs as field emitters in hydrogen gas. An extremely high luminance of $10^6$ cd/m$^2$ is achieved for ZnS/Cu/Al green phosphor as a cathode with a DC voltage of 30 kV and a DC current of 400 μA. The ultrahigh luminance light source is expected to emit luminous flux of more than 1000 lm [397]. These data are comparable to those of CRT-based lamps. For CRT light-emitting-based electric lamps with various colors, the current density at the cathode is 10 mA/cm$^2$, the average electric field intensity is $1.5 V/\mu m$, and the luminance of elements of various colors range from $1.5 \times 10^4$ to $6.3 \times 10^4$ cd/m$^2$ [388].

The last kind is the planar incandescent light source consisting of CNT sheets [264]. CNT sheets are usually fabricated by the dry-spinning method described in Section 2.2.3.2. Figure 59 shows such a planar lighting source. Pure CNT sheets are connected to two electrodes. When
current passes through the CNT sheets, the CNTs are heated up to over 1000°C in less than 1 ms and then emit light.

4.1.5. Field-emission flat-panel displays

In conventional field-emission displays, metal tips with micron sizes have usually served as emission sources. When a voltage is applied between a gate electrode and a metal emitter, a higher electric field is generated at the apex of a metal tip, inducing electron emission from the metal tip. Emitted electrons are accelerated toward an anode and bombard a phosphor layer, producing visible light. Such metal field-emission displays perform as cathode ray tube (CRT)-like displays but their production cost is higher.

CNTs have been spotlighted as one of the promising alternatives for new electron sources used in flat field-emission displays, due to their superior emission properties as discussed in Section 4.1.3 and their straightforward fabrication processes. CNTs are expected to produce field-emission displays with low cost, low power consumption, and high scalability [398]. Now flat-panel display is one of the most lucrative CNT applications being developed in the commercial sector.

CNTs provide high current densities, stable emission, long lifetimes, and low emission threshold potentials [359,388]. Current densities as high as 4 A/cm² have been obtained, compared with the 10 mA/cm² needed for flat-panel field-emission displays [399]. The short-term emission of CNT emitters is stable with a current density of 1 mA/cm² and a fluctuation of 2% without bias resistors. This emission current is sufficient for practical use in flat-panel displays. A lifetime exceeding 10,000 h is suggested under direct current driving and continuous electron emission without diminution [394]. These reliable results, i.e., high current densities and long-time stability, enable the commercialization potentials of large-area full-color flat-panel displays using CNT emitters in the near future.

Based on the emission properties of the aligned CNT arrays, a series of flat-panel displays have been designed. The first CNT-based flat-panel display consisting of 32 × 32 matrix-addressable pixels was reported in 1998 using random CNTs as the electron emission source [400]. Later, 4.5” [401,402] and 9” [398] colorful field-emission displays have been reported. At present, flat-panel displays based on CNT field-emission cathodes are developed in hundreds of laboratories, and commercial displays have already been manufactured. The CNTs in the commercial flat-panel displays are usually vertically aligned on cathode electrodes for better electron emission.
present, CVD technologies are employed to synthesize vertically aligned CNTs over a large area of substrates, as discussed in Section 2.1 and Section 3.

Figure 60(a) shows a basic structure of a flat-panel display based on CNTs. CNTs are vertically grown on a substrate in the form of bundles, working as the cathode electron source. Indium tin oxide (ITO) is deposited on glass as the anode. By applying a bias voltage across the CNTs and the ITO anode, electrons are emitted from CNT tips and bombard onto the phosphor screen to emit light. Figure 60(b) illustrates an image produced by a CNT-based color flat-panel display.

The commercial flat-panel displays have more complex structures. Figure 61 shows a double-gated CNT display. The emitted electrons are focused by a focusing electrode before arriving at the phosphor layers.

Compared with liquid crystal displays, the field-emission displays have a lower power consumption, a higher brightness, a wider viewing angle, a higher response rate, and a wider operating temperature range [318].

4.1.6. Incandescent displays

Besides the field-emission displays, CNT array displays can also be fabricated based on incandescence mechanisms [403]. Figure 62 illustrates an incandescent CNT array display fabricated...
from a CNT cloth. The CNT cloth is fabricated from aligned CNTs by the dry-spinning method (see Section 2.2.3.2). The superaligned CNT cloth (Figure 62(a)) is suspended on the screen-printed electrodes of several tens of microns (Figure 62(b)). Then the CNT cloth is cut into separate 100 μm × 300 μm units (Figure 62(b)) as display pixels using a laser. When a current is applied through the cloth film on the electrodes, the CNT film is heated to incandescence in vacuum, as discussed in incandescent light (Section 4.1.4) and observed in the macro-CNT cloth [404].

The maximum brightness of an individual pixel is 6400 cd/m² at about 0.08 W heating power. The current and incandescent brightness stabilities of a pixel are 0.05 and 1.1%, respectively, at 1740 K. Figure 62(c) shows an image of one Chinese word displayed by the incandescent 16 pixel × 16 pixel array.

The lifetime of the CNT incandescent display is estimated to be about 550 h because of the evaporation of CNTs at high temperature. Compared with field-emission CNT displays, the turn-on voltage of the CNT incandescent displays is about 4–7 V, the response time is less than 1 ms, and there is no viewing-angle problems of LCDs.

4.1.7. X-ray generators

When the field-emitted electrons from CNT tips bombard onto a metal target, not a phosphorescent screen, X-rays are emitted instead of light [405]. Figure 63(a) illustrates a circuit of X-ray CNT generator. The field-emitted electrons from CNT tips bombard on the Cu target to produce X-ray. The X-ray intensity increases exponentially with the linear increase in accelerating potential. When the CNTs are uniform, the emission energy distribution of emitted electrons is far more uniform than for thermal electrons [405]. This near uniformity in electron energy provides higher resolution than thermionic electron sources do (Figure 63(b)).
4.1.8. Microwave devices

The CNT arrays can also be constructed into a microwave diode [406], as shown in Figure 64. The CNT arrays consist of uniform individual CNTs (average diameter of 59 nm and height of 5.5 μm) with a spacing of twice the CNT height. The CNTs can be grown by the PECVD method and a catalytic pattern can be prepared by the e-beam lithography, as discussed in Section 2.1.3.2. Such diodes can operate at 1.5 GHz or even 32 GHz, holding promises for a new generation of compact microwave devices for telecommunication.

4.2. Optical devices

CNTs (with or without a surface coating) can interact with light strongly due to their nanoscale dimensions. The interaction is contributed to either Mie resonances or plasmonic resonances when the frequency of light is close to the CNT surface plasmon frequencies. When an array of aligned CNTs of uniform sizes is incident with light, each CNT can be viewed as physically identical elements. The intra-CNT factor (interacting with light as individuals) and the inter-CNT factor (interacting with light as pairs or groups) will play a role in the overall interaction behaviors of the CNT array. These two factors can be adjusted by using arrays of different inter-CNT spacings and periodicities, to purposely suppress the other factor. More specifically, the inter-CNT factor is suppressed when the CNTs have a random spatial distribution among each other, where it is suitable to observe the intra-CNT factor in optical antennas and classical nanocoaxes. The intra-CNT factor is suppressed when the CNTs are arranged periodically in space where the inter-CNT factor prevails in the overall characteristics (2D photonic crystals, distributed nanocoaxes, etc.). The semiconducting CNTs can also interact with light to generate photo-induced carriers in a photoelectric process and can be used in photoelectrochemical solar cells [407], but such effects would not significantly benefit from CNT alignment and are therefore beyond the scope of this review.

The aligned CNTs used for optical devices are 3D ordered. Such 3D ordered CNTs are usually fabricated by the PECVD method described in Section 2.1.3.2.

4.2.1. Photonic crystals

It was reported that periodic arrays of aligned CNTs diffract light, behaving as polaritonic crystals with formation of polaritonic and photonic band gaps [35]. The photonic crystal behaviors lie in the high aspect ratio of individual CNTs, their alignment, and their wavelength-scale periodic
distribution in the plane perpendicular to their alignment which causes high-contrast periodic modulations of the dielectric function of the system \cite{280,408–412}.

Figure 65(b) shows a laser diffraction pattern obtained from an aligned CNT array of hexagonal periodicity and lattice parameters close to the visible wavelengths (Figure 65(a)). The diffraction pattern was obtained by a shining green (560 nm) and a blue (454 nm) laser light perpendicular to the plane of the lattice, and collecting the projection onto an almost flat screen, which allowed for an observation of a large portion of the projected reciprocal space but caused a distortion of the triangular symmetry of the pattern. Apart from this, the pattern is highly rotationally symmetric (except for the third-order blue diffraction spots), showing that the scatters (nanotubes) are circularly symmetric in the plane. Note that there is a rather small hexatic distortion of the pattern, indicating the presence of a possible formation of misaligned crystalline macro regions. There is also a small diffusive scattering (nonzero Ursell function) resulting from the fact that the nanotubes are not perfectly straight (see Figure 65(a)). For perfectly straight CNTs, the diffraction spots would be points and the green background around the central spot would disappear. The amount of the spot broadening can be estimated using the Debye–Waller factor and assuming that bent nanotubes can be viewed as effectively displaced from the lattice sites. The inset in Figure 65(b) shows the diffraction pattern for a red light (680 nm), obtained at an incidence
Figure 65. (a) Periodically aligned CNTs arrays. (b) Diffraction pattern of laser light at different frequencies by the nanotube arrays shown in (a). The CNT height is 1 μm. Inset: diffraction pattern of red laser light. Reprinted with permission from K. Kempa et al., Nano Letters, 3, pp. 13–118, 2003 [35]. Copyright (2003) American Chemical Society.

angle of 45°. Note that there is an asymmetry of the spot intensity favoring the forward reflection. This reflects the fact that with increasing angle of incidence, the diffraction pattern must evolve into the in-plane scattering, which according to the Laue construction should consist of only one diffraction spot for a given incoming direction.

The CNTs can be coated to extend the variation scopes of the photonic crystal parameters. They can also be used as structural templates to obtain nonmetallic photonic arrays, including nonmetallic 2D bandgap crystals [35].

4.2.2. Optical antennae

When individual CNTs in an aligned array have lengths of a few hundred nanometers (wavelength of visible light in air), the array interacts with visible light so strongly that the reflection spectrum shows a series of peaks depending on the CNT length. Such interaction is due to the excited oscillation of the free electron gas of the CNTs by the electromagnetic field, which may further develop into a resonant state if the CNT length (i.e., the cavity length of the electron oscillation) matches the field wavelength such that \( L = \frac{m \lambda}{2} \), where \( m \) is an integer.

This is in great analogy with conventional dipole antennas reacting with radio waves except that here the operating frequency is much higher (optical frequencies). The CNTs therefore belong to the scope of optical antennas where metallic nanostructures show high scattering/absorption efficiencies with incident light. The alignment of the dipole optical CNT antennas in an array allows the orientation features in the reflection of individual CNT antennas to be preserved in the reflection of the macroscopic array. This means that the polarization effects of a dipole antenna, i.e., the antenna response is strong when the incident light is polarized in the antenna length direction, and suppressed in the perpendicular direction, can be fully observed on the array composed of millions of individual dipoles. Indeed, this is the case (shown in Figure 66) as one observes the sinusoidal variation of the reflection intensity as the incident polarization is rotated with respect to the CNT length orientation [413].

The angular radiation patterns of aligned CNT antennas (Figure 67) have also been recorded using arrays of lower areal densities and of different CNT lengths. Again, the alignment of the arrays allows for the probing of individual CNT characteristics. Using a projection method, the reflection patterns of CNT antennas show consistency with dipole or multipole antenna theories where multiple intensity lobes are confirmed and related to the antenna length. The discovery
that arrays of aligned CNTs can work as optical antennas reveals tremendous potentials in future applications in optical and optoelectronic devices, such as optical polarizers, detectors, and solar cells which will be further discussed in the following sections.

4.2.3. Optical waveguides

CNT coaxial cables (Figure 68) can waveguide visible light. These nanocoaxes are optically long but have subwavelength channel with and they strongly transmit light in the entire visible frequency range without a frequency cutoff. With judicious choice of materials, the propagation is essentially via the conventional transmission electromagnetic mode of a common coaxial cable.

Figure 69 shows the results of optical reflection from, and transmission through, a nanocoax array (see Figure 68) [414]. In Figure 69(a), white light is reflected from the top surface of the sample, showing the topography, with dark spots due primarily to absorption of light by the nanocoaxes. When the light is incident from the backside, it is absorbed and transmitted along the coaxes and emerges at the top surface, as seen by the spots in Figure 69(b) for the same region of this sample. Note that the transmitted light remains white, suggesting that there is no cutoff frequency. The inset in Figure 69(a) shows an SEM image of a nanocoax used for the experiment.

More experiments indicated that a laser beam (\(\lambda = 680\) nm) can transmit directly through the nanocoax array and the transmission is independent of nanocoax length [414]. Transmission at \(\lambda = 532\) nm was obtained for various sample thicknesses (i.e., coax lengths). This length independence is fully consistent with the theoretical value for the photon propagation length (50 \(\mu\)m), which is

![Figure 66. Polarization effect. Reflected, normalized light intensity versus polarization angle \(\theta\) for the sample shown in the insets. Circles represent the light intensity from the random array of nanotubes, and squares from the metallic film. Lines represent the expected functional dependencies: \(I = \cos^2 \theta\) for nanotubes (solid), \(I = \sin^2 \theta\) for the metallic film (dotted). Left inset: sample viewed with the polarization plane parallel to nanotubes (\(p\)-polarization), \(\theta = 0^\circ\). Right inset: sample viewed through polarizer with the polarization plane perpendicular to nanotubes (\(s\)-polarization), \(\theta = 90^\circ\). Scale bars: 1 cm. Reprinted with permission from Y. Wang et al., Applied Physics Letters, 85, pp. 2607–2609, 2004 [413]. Copyright (2004), American Institute of Physics.]
much greater than each film thickness. There is also no cutoff frequency. The nanocoax medium is expected to process transmitted light in a discrete manner by breaking the incoming plane wave into wavelets, transmitting it to the other side, and then re-assembling the plane wave on the other side of the medium. For straight, identical coaxes, the re-assembled wave retains all
the propagation characteristics of the incoming wave. This explains the observed lack of beam divergence.

By replacing the inter-electrode dielectric with a nonlinear material in each nanocoax, one may achieve light mixing, switching, or phase conjugation. The nanocoax structures described here can be fabricated from a wide variety of materials. The inner and outer conductors can be
made from any appropriate metal, using soft (e.g., templated electrodeposition, CVD) or hard
(electron or focused ion beam lithography) techniques, and the choice of dielectrics is extensive
[414]. Moreover, the coupling of radiation (light) to the nanocoax can be achieved in ways other
than the linear antenna described here.

4.2.4. Solar cells based on nanocoaxes
The particular geometry of aligned CNTs allows a layer-by-layer deposition strategy to fabricate
an array of nanocoaxes of various thin films in the CNT radial direction. One typical application
example of such nanocoax structures is a new type of solar cells where active photoabsorbers
such as p–i–n amorphous silicon thin films are sandwiched between two coaxial metallic layers
(Figure 70). This variation of the conventional thin-film amorphous silicon solar cell structure
may allow separation of the photonic absorption length in the absorber from the photoexcited
carrier collection distance to achieve superior energy conversion efficiencies [415]. The fabricated
structure utilizes a distributed nanocoax scheme where, unlike in the classic nanocoax scheme
[414,416], each individual nanocoax does not have an opaque outer conductor shell, while the
metallic cores of the neighbor nanocoaxes function effectively as its outer shell. Indeed, clear
photocurrent enhancement has been observed in these nanocoax solar cell structures using very
thin absorber layers (∼180 nm). It should be pointed out that in these devices, the aligned CNTs are
mostly structural templates where consecutive metallic and semiconducting layers are deposited
onto. The low-cost nature of the CNT growth process gives the aligned CNTs an advantage over
other similar templates such as etched single-crystalline silicon wafers.

The power conversion efficiency of an exemplary nanocoax solar cell (0.18 cm² total area) is
\( \eta = 6.1\% \). As demonstrated in Figure 70(c), this performance well exceeds (about 50% higher)
the efficiency of a planar cell with similar absorber thickness (\( \eta = 3.3\% \)) [415].

Similar solar cell fabrication schemes can be employed at a larger scale where towers made of
multiple aligned CNTs can be used as templates to deposit the following thin-film solar cell layers
(Figure 71). The efficiency can be doubled from 3.5% in a planar configuration to 7% in the CNT
tower configuration at 45° solar incidence with CdTe thin film absorbers (Figure 71(a)). In another
instance, a short-circuit current enhancement of 25% has been achieved over the conventional

Figure 70. CNT nanocoaxes. (a) Planview SEM image of CNT nanocoaxes. (b) Cross-sectional SEM image
of FIB-cut CNT solar cell. (c) Photovoltaic performance of the CNT solar cell. Reprinted figure with per-
[415]. Copyright John Wiley and Sons.

planar structure, owing to the highly effective light-trapping structure of the coaxial MWCNT/a-Si:H nanowire array (Figure 71(b)) [418]. In this case, the nanocoax effect is absent due to the large dimensions of the structures and the performance enhancement is purely expected from the enlarged surface area of the absorber material and the higher ray scattering frequency for broad incident angles due to the 3D geometry.

4.3. Nanoelectrode-based sensors

Individual CNTs can be semiconducting or metallic, and are good candidates for electrode materials. So CNT arrays have been fabricated into nanoelectrode arrays for various applications. In this section, we review the CNT nanoelectrode arrays and their applications.

4.3.1. Nanoelectrode arrays

Microelectrode arrays consisting of hundreds of metal microelectrodes with diameters of several micrometers have been fabricated by lithographic techniques [419]. The microelectrodes show many advantages over the conventional macroelectrodes such as high mass sensitivities, enhanced mass transport, and a decreased influence from the solution resistance. Further size reductions of each individual electrode to nanometers and an increase in the density of electrodes can improve the detection limits and the signal-to-noise ratio [170] since the noise level depends on the active area of the individual electrode, whereas the signal strength depends on the total area of the electrodes [420]. Such 2D nanoelectrode arrays have been fabricated based on gold nanowires [421].

SWCNTs exhibit high electrical conductivities and are the most promising candidates for miniaturizing electrodes beyond the micrometer-scale currently used in electronics. Up to now, CNT-based nanoelectrodes have already been fabricated [422–431].

CNT nanoelectrode arrays are fabricated with aligned CNTs of low site densities. Such aligned CNTs can be grown by PECVD method from catalytic patterns, as described in Section 2.1.3.2. To make each CNT working as an individual nanoelectrode, the spacing needs to be sufficiently larger than the CNT diameters to prevent the diffusion layer from overlapping with the neighboring electrodes [432,433]. Based on these low-site-density CNTs, nanoelectrode arrays consist of millions of nanoelectrodes (with each electrode being less than 100 nm in diameter). Because the total current of the loosely packed electrode arrays is proportional to the total number of individual
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Figure 72. Fabrication scheme of the nanoelectrode arrays. (a) Ni nanoparticle electrodeposition. (b) Growth of aligned CNT. (c) Coating of SiO2 and M-bond. (d) Polishing to expose CNTs. Reprinted with permission from Y. Tu et al., Nano Letters, 3, 2003, pp. 107–109 [170]. Copyright (2003) American Chemical Society.

The fabrication of CNT nanoelectrode arrays has been described in existing literatures [170, 178,434]. Figure 72 shows the SiO2/epoxy-coated nanoelectrode arrays. The CNTs are directly grown on the conductive substrate to ensure good electrical conductivity to the external circuit. In a typical experiment, Ni catalytic nanoparticles are electrodeposited on a Cr-coated Si substrate of 1 cm² in area (Figure 72(a)). The site density of the catalytic nanoparticles is low. Aligned CNT arrays are then grown from those Ni nanoparticles by PECVD (Figure 72(b)). Next, the CNT spacings are filled by epoxy spin-coating or various other coating methods (Figure 72(c)). In a typical filling process, an epoxy-based polymer with a curing agent is spin-coated on the substrate and covers up to half of the CNT length. The protruding parts of the CNTs are mechanically removed subsequently by polishing (Figure 72(d)).

Figure 73 shows the SEM images of the CNT nanoelectrode array fabrication steps corresponding to the scheme shown in Figure 72. The bright dots in Figure 72(a) are the electrodeposited Ni nanoparticles that are randomly distributed on the substrate. Figure 72(b) shows the low density aligned CNT array grown by PECVD from the Ni nanoparticles. Figure 72(c) shows the morphology after coating with a thin layer of SiO2 followed by a second layer of epoxy film. The electrodes, the number of electrodes totaling in the millions is highly desirable. The size reduction of each individual CNT electrode and the increased total number of CNT electrodes result in improvements in both the signal-to-noise ratio and the detection limits of CNT array-based nanoelectrode arrays [420,421].
Figure 73. Scanning electron microscope images of CNT nanoelectrode array fabrication. (a) Top view; (b–f) from a 45° side view. All of the scale bars represent 5 μm. (a) Electrodeposited Ni nanoparticles. (b) Low-site-density-aligned CNT array. (c) CNT array coated with SiO₂ and an epoxy layer. (d) Close-up look at a single half-embedded CNT. (e) CNTs after polishing. (f) Second electrodeposition of Ni nanoparticles on the broken CNT tips only. Reprinted with permission from Y. Tu et al., Nano Letters, 3, 2003, pp. 107–109 [170]. Copyright (2003) American Chemical Society.

CNT arrays are half-embedded in the polymer. Figure 72(d) provides a close-up look at a single half-embedded CNT. Figure 72(e) shows the topography after mechanical polishing. It is clearly shown that only the tips of the embedded CNTs are exposed. To prove that the tips of the CNTs are exposed and conducting, electrodeposition of Ni nanoparticles is repeated. Figure 72(f) shows that the Ni nanoparticles are deposited only on the CNT tips, nowhere else. This also indicates that the carbon nanoelectrode array could be used as a template to fabricate other metal nanoelectrodes.

For successful fabrication of nanoelectrode arrays, two important requirements exist. First, the inter-spacing of the individual electrodes should be much larger than the radius of each electrode; otherwise, a closely packed nanoelectrode array will behave similarly to a macroelectrode due to the diffusion layer overlap [419,435–439]. The cyclic voltammogram measurements indicate [434] that there is no diffusion layer overlapping between the nanoelectrodes when the CNTs are separated from their nearest-neighbors by at least 5 μm, which is much larger than the diameter of each CNT (50–80 nm). Therefore, controlled low site density of aligned CNTs is the key for the fabrication of CNT nanoelectrode arrays, which can be done by tuning the site density of Ni
Figure 74. Cyclic voltammetry curve of the carbon nanoelectrode arrays. The curve was taken in a solution of 4 mM K$_3$Fe(CN)$_6$ in 0.5 M KNO$_3$. The scan rate was 40 mV/s. Reprinted with permission from Y. Tu et al., Nano Letters, 3, 2003, pp. 107–109 [170]. Copyright (2003) American Chemical Society.

nanoparticle catalysts, using an electrochemical deposition method [178]. Secondly, there must be a passivation layer that can protect the underlying conducting layer as well as prevent current leakage and corrosion. Both inorganic materials, such as SiO$_2$ and Si$_3$N$_4$, and organic materials, such as epoxy and photo resist, have been previously tested [440]. The ideal passivation layer is captive and crack-free, long lasting in aqueous electrolyte solutions, adhering well to substrates and electrodes, mechanically strong, and easily processable. Insulating materials should be good enough to prevent the current leakage that results in the distortion of the cyclic voltammetry curve. Very low background current and leakage current are achieved when the CNT arrays are excellently sealed by the spin-coated epoxy resin, which enables the sensitivity analysis [434].

The cyclic voltammetry curve of the CNT nanoelectrode arrays (Figure 74) indicates that the signal (in the range of microamperes) generated from the nanoelectrode arrays is much larger compared to the signal (a few picoamperes) generated from a couple of carbon electrodes with a similar disk shape [441] because the total current for the loosely packed electrode array is proportional to the number of individual electrodes [433].

To date, many research groups have fabricated CNT nanoelectrode arrays [170,429,435,441]. These are based on the advantages of CNT materials over conventional macroelectrodes such as enhanced mass transport and decreased influence from the solution resistance, which makes an excellent electrochemical transducer in various applications. The aligned CNT nanoelectrode has a high mass sensitivity, an increased mass-transport rate, a decreased influence from the solution resistance, and a higher signal-to-noise ratio, leading to a much lower background current than other electrode configurations. For example, the CNT array of nanoelectrodes can produce a much higher current than a single nanoelectrode [442] and bundles of CNTs [443,444], which can improve the signal-to-noise ratio.

The nanoelectrodes have many practical applications such as ultrasensitive electrochemical sensors for chemical and biological sensing. Below we will review some of these applications.

4.3.2. Ion sensors

The unique electronic, chemical, and mechanical properties of CNTs make them extremely attractive for applications in chemical and biochemical sensors [318,445]. Most CNT sensing platforms
take advantage of the unique properties of CNTs, such as increased electrode surface areas [446] and high electron transfer rates [447]. It is well known that the electron transfer rate of the electrode is dominated by its surface structure. The sidewall atomic structure of MWCNTs is similar to the graphitic basal plane and the open-end of CNTs is similar to the edge-plane. Because the electron transfer on edge-plane graphite is faster than that on the basal-plane graphite, the open ends of the CNTs have higher electron transfer rates similar to a graphitic edge-plane electrode [448], while the sidewalls exhibit very low electron transfer rates similar to the graphitic basal plane. It is reported that the high-site-density CNT array and CNT forest show fast electron transfer characteristics [447,449].

The CNT forest electrodes or high-site-density CNT arrays do not act as individual nanoelectrodes because the high site density of the CNTs causes the overlapping of diffusion layers of individual nanoelectrodes, as discussed in Section 4.1.1. So the low-site-density CNT arrays are employed as CNT ion-sensing platforms. To make each CNT work as an individual nano-electrode, the spacing needs to be sufficiently larger than the CNT diameter to prevent diffusion layer from overlapping with the neighboring electrodes. The microsphere lithography method is a good technique to prepare nanoparticle catalysts with low site densities. The electrodeposition method is also suitable to prepare such catalysts for low-site-density growth. In order to take advantage of a high electron transfer rate, the CNT tips are always opened. To eliminate the background current leakage generated from the sidewalls of CNTs and the electrode capacitance, the sidewalls are sealed with an epoxy passivation layer. Such a structure provides a high signal-to-noise ratio.

The CNT sensing platforms are fabricated similarly to nanoelectrode arrays, as shown in Figure 72. In a typical process, a CNT array is grown first by PECVD [429]. The site density of the aligned CNTs is controlled by tuning the site density of catalytic nanoparticles. The site density is typically $1 \times 10^6$ cm$^{-2}$, depending on the final length of CNTs. An epoxy resin layer of microns thick is coated on the aligned CNT arrays grown on the substrate surface using a standard spin-coating method. The aligned CNTs show very good mechanical stabilities and preserve their vertical alignment. The CNTs are half-embedded in the resin with 2–3 μm of length protruding from the resin surface. By using a lens paper to gently polish the coated CNTs, the protruding parts are broken and removed by ultrasonication in water. Then an electrical connection is made to the CNT substrate to produce an ion-sensing platform.

Square-wave voltammetric measurements are carried out in an electrochemical cell containing a CNT-array working electrode, a Ag/AgCl reference electrode, and a platinum wire counter-electrode. A magnetic stirrer together with a magnetic bar provides the convectional conditions when needed.

Compared to the traditional macroelectrode, the aligned CNT nanoelectrode has a high mass sensitivity, an increased mass-transport rate, a decreased influence from the solution resistance, and a higher signal-to-noise ratio, leading to a much lower background current. The CNT array sensing platform shows potential to detect very low concentrations of heavy metal ions compared to a traditional bulk and macro-electrode sensing platform [450].

Figure 75(a) presents a typical square voltammogram for a mixture containing 5 μg/l cadmium and lead ions. A well-defined, undistorted, sharp signal with a favorable resolution is obtained. The peak potentials of cadmium and lead are $-0.75$ and $-0.55$ V, respectively. The stripping signal for the selected target metals is surrounded with low background contributions, indicating effective sealing on the sidewalls of CNTs during the preparation of the nanoelectrode array. The very attractive signal-to-noise characteristics and peak resolution indicate that the aligned CNT array can be used as an excellent electrochemical sensing platform [450].

Figure 75(b) displays the square voltammogramic response of an aligned CNT array for increasing cadmium ion concentrations under the optimum experimental conditions. Well-defined peaks, proportional to the concentration of the corresponding cadmium, are observed. A linear relationship
Figure 75. (a) Typical square wave voltammogram of 5 μg/l cadmium and lead in 0.1 M acetate buffer (pH 4.5) in the presence of 500 μg/l bismuth. (b) Square wave voltammogramic response of cadmium solution with increasing concentration (0.5, 1, 2, 4, 6, 8 μg/l). The small shoulder peaks at −0.57 V are attributed to a trace of lead in the blank solution. A square-wave voltammetric scan with step potential: 5 mV; amplitude: 20 mV; and frequency: 25 Hz. G Liu et al., Analyst 130, pp. 1098–1101, 2005 [450] – Reproduced by permission of The Royal Society of Chemistry.

between the stripping current and cadmium concentration is obtained covering the concentration range from 0.5 to 8 μg/l, as the linear regression equation being \( I(nA) = 37.054 \times \text{concentration (μg/l)} - 10.486 \), with a correlation coefficient of 0.9955. The detection limit is improved significantly by increasing the accumulation time. A detection limit of 0.04 μg/l (40 ppm) is estimated on the basis of an \( S/N = 3 \) characteristic of the 0.1 μg/l data points in connection with a 240-s accumulation time. Such improvement of the stripping signal and extremely low detection limit benefit from the high signal-to-noise ratio of CNT arrays.

Lead is regarded as a highly toxic metal ion to a wide variety of organs in both human and animals, including nerves, immune, reproductive, and gastrointestinal systems. The ability to rapidly detect a trace amount of Pb^{2+} species on-site is very desirable. Figure 76 shows that the voltammetric response is a linear function of Pb^{2+} concentrations ranging from 2 to 100 ppb [429]. The lead concentration can be detected at a very low level. The inset shows the response peaks of 2 to 100 ppb of Pb^{2+}.

4.3.3. Gas sensors

A chemical sensor can be defined as a device that responds to changes in the local chemical environment. The response should be predictable such that it scales with the magnitude of change in
the environment. Additionally, a chemical sensor should be sensitive and selective to the chemical molecule concerned. CNTs are good candidates for chemical detection, because the nanoscale dimensions and exceptionally large surface area of CNTs make them more environmentally sensitive than bulk carbon materials. To date, CNTs have shown sensitivities toward gases such as NH₃, NO₂, H₂, C₂H₄, CO, SO₂, H₂S, and O₂, and most of these demonstrated sensors are fabricated from random or individual CNTs in the configurations of CNT-based field-effect transistors [303,308,451,452]. The aligned CNTs can be 1D ordered, directly grown on random catalysts by PECVD method (see Section 2.1.3.1) or by thermal CVD method (see Section 2.1.1), or be 3D ordered, grown from 2D ordered catalysts by PECVD method (see Section 2.1.3.2).

There are two kinds of CNT array gas sensors. One is the two-terminal gas sensor (Figure 77(a)) and the other is three-terminal, as shown in Figure 77(b). The two-terminal sensors are simple,

![Figure 76](image1.png)

**Figure 76.** The voltammetric response (current) of Pb²⁺ in 0.1 M NaNO₃ solution as a function of Pb²⁺ concentration, measured after 3 min of deposition. Pulse amplitude: 25 mV; step amplitude: 5 mV; frequency: 100 Hz. The voltammograms correspond to Pb²⁺ concentration of 2, 5, 25, 50, and 100 ppb. Reprinted figure with permission from Y. Tu et al., Electroanalysis, 17, 2005, pp. 79–84 [429]. Copyright John Wiley and Sons.

![Figure 77](image2.png)

**Figure 77.** Schematic cross-section views of (a) two-terminal and (b) three-terminal CNT gas sensors. (a) Reprinted from Sensors and Actuators B: Chemical, 93, Y.M. Wong et al., pp. 327–332. Copyright (2003), with permission from Elsevier. (b) Reprinted from Diamond and Related Materials, 14, C.S. Huang et al., pp. 1872–1875. Copyright (2005), with permission from Elsevier.
while the sensitivity of the three-terminal sensors is higher. Let us review these gas sensors as follows.

CNT-based gas sensors were demonstrated as early as in 2000 when the responses of CNT field-effect transistor, mainly made of a single semiconducting SWCNT, to NO₂ and NH₃ gases were reported [303]. NH₃ exposure resulted in a shift in the transfer characteristic gate voltage of approximately -4 V, while NO₂ exposure created a shift of approximately +4 V. Alternatively, when the transistor was held at a constant gate voltage of $V_G = 0 \text{ V}$, exposure to NH₃ resulted in a decrease in the device current, while NO₂ exposure ($V_G = +4 \text{ V}$) resulted in an increase. The response time to 200 ppm NO₂ was a few seconds, and the sensitivity, defined as the resistance after exposure divided by the initial resistance, was approximately 100–1000. The response time to approximately 1% NH₃ was a few minutes with a sensitivity between 10 and 100. A floodgate of interests in the development of CNT-based gas sensors was generated by these initial results of CNT gas-sensing capabilities. Up to now, more than 1000 reports focused specifically on the application of CNTs in gas sensors have been published [455]. The gas and vapor sensors made of individual CNTs or CNT networks are well reviewed recently [455–461]. Some CNT array sensors are also reviewed recently [459]. Here we focus on the application of CNT arrays in gas and vapor sensors.

CNT array gas sensors have an outstanding sensitivity at low temperatures of fast response and high selectivity [462]. Several types of gas sensors using CNTs have been proposed. One is the gas ionization sensor, in which CNTs are used as field-emission electrodes to ionize the analyzing gas, resulting in high gas selectivity and sensitivity [463]. Another type is based on a change of the electrical conductance of CNTs when adsorbing gas molecules. The mechanism of the CNT gas sensors is based on the dependence of CNT electrical resistance with ambient gas concentration. When the p-type semiconducting CNTs adsorb oxidizing molecules, electrical resistance of the CNTs decreases with the number increase of the adsorbed gas molecules. In other words, the electrical conductance of p-type semiconducting CNTs is modified by the electron transfer between CNTs and oxidizing or reducing gas molecules adsorbed on the CNT surfaces. The second type of gas sensors has extremely high sensitivity and fast response at room temperature and is compatible with integrated circuit fabrication.

### 4.3.3.1 Hydrogen gas sensors

The risk of explosion is the primary reason for the needs to accurately measure H₂ levels since concentrations as low as 4% in air can become explosive. Bare CNTs do not show appreciable sensitivity to H₂ due to the weak binding energy of hydrogen to the surfaces of CNTs [464]. After being decorated or functionalized by Pd or Pt nanoparticles on their sidewalls, the CNTs can detect the ppm level of H₂ gas [465,466]. It is believed that H₂ dissociates into atomic hydrogen on the Pd or Pt nanoparticle surface at room temperature to form PdH₂ or PtH₂, decreasing the Pd or Pt work function and leading to electron donation into the CNTs from the nanoparticles [467,468]. As a result, the electrical conductance of the Pd-decorated SWCNT decreases, yielding a response time of a few seconds.

Figure 78(a) shows an SEM image of a vertically aligned CNT array grown in an AAO (anodized aluminum oxide) template used for room-temperature detection of ppm concentrations of H₂. The CNTs are coated with a Pd film to form a two-terminal gas sensor to enhance the sensitivity of the H₂ detection. The electrical resistance varies with the concentration of H₂ (Figure 78(b)). The Pd-coated CNT array sensor is sensitive to hydrogen gas concentrations from 100 ppm to 1.5% at room temperature.

H₂ is also detected by a Pd/MWCNTs/n-Si thin-film sandwich structure [453]. The thin layer of Pd is sputtered on top of the MWCNT array. The current is reduced in the presence of hydrogen and the reduction is attributed to an increase in the barrier height between the Pd-CNT interface after H₂ adsorption.
Figure 78. (a) Aligned CNT array grown from an AAO template. (b) Response of a CNT array coated with a Pt film to H$_2$ exposure expressed as the relative change of electrical resistance $\Delta R/R_0$ at zero gate voltage. Reprinted from Sensors and Actuators B: Chemical, 124, D. Ding et al., pp. 12–17. Copyright (2007), with permission from Elsevier.

4.3.3.2 Nitrogen gas sensors  The electrical resistance of CNTs is found to increase when CNTs are exposed to the reducing N$_2$ gas [470]. Figure 79(a) shows the electrical resistance variations of a three-terminal sensor consisting of CNT arrays upon exposure to an N$_2$ filling and pumping environment. After CNT arrays are grown on a SiO$_2$/Si substrate from patterned catalysts, the silicon substrate on the backside acts as the gate of the sensor. The structure of the sensor is shown in Figure 77(b). Source and drain electrodes are biased at 10 V with zero gate voltage. Since N$_2$ is a reducing gas [470], CNTs receive electrons due to a N$_2$ absorption process and the concentration of conducting holes on the CNTs decreases. As a result, the electrical resistance between source and drain electrodes increases. A higher N$_2$ pressure makes the electrical resistance higher. Because the N$_2$ is absorbed on CNT surfaces by van der Waals forces, almost all the N$_2$ molecules leave CNT surfaces after pumping and the electrical resistance returns to its initial value.

Experiments indicate that the gas sensor sensitivity increases with higher source drain bias voltages. Furthermore, the sensor sensitivity is also affected by the gate voltage. Figure 79(b) shows that the electrical resistance of a CNT array changes with various gate voltages at a fixed

Figure 79. Electrical resistance of a three-terminal gas sensor. (a) The electrical resistance between the source and the drain at 10V bias voltage without any gate voltage under various N$_2$ filling pressure from 50 mTorr to 500 Torr. (b) The electrical resistance of a CNT array measured at a fixed 5V source–drain bias voltage while applying various gate voltages under a 5 Torr N$_2$ pumping and filling environment. Reprinted from Diamond and Related Materials, 14, C.S. Huang et al., pp. 1872–1875. Copyright (2005), with permission from Elsevier.
5V source–drain voltage in a 5 Torr N₂ pumping and filling environment. The initial electrical resistance increases when a positive gate voltage is applied and decreases with a negative gate voltage. The resistance of CNT array restores its initial value after a cycle of N₂ filling and pumping under different positive and negative gate voltages. The sensor sensitivity increases with the decrease in the gate voltage from positive to negative due to the increase in the gas-binding sites caused by a negative gate voltage.

4.3.3.3 Nitrous oxide gas sensors  Nitrous oxides such as nitrogen monoxide (NO) and nitrogen dioxide (NO₂) are typical air pollutants that cause environmental problems. There are demands for small and cheap gas sensors for NO detection in medical applications and scientific research.

Figure 80 shows a two-terminal gas sensor with interdigitated electrodes. The platinum interdigitated electrodes are deposited on the CNT arrays to provide larger sensing areas and sufficient contact areas between the electrodes and the coated CNTs. The resistance change of CNTs under gas exposure is detected by two-terminal resistors with a DC voltage. NO₂ exposure drastically decreases the electrical resistance of the CNT arrays and completely removing the gas exposure restores the initial resistance of CNT arrays. The conductance change of the sensors shows a linear response to the gas concentration upon exposure to NO₂, no matter MWCNT arrays [471] or SWCNT arrays [435] are used.

Besides NO₂, NO can also be detected using gas sensors with identical structures [471,472].

4.3.3.4 Ammonia gas sensors  In the case of chemical gas sensors based on electrical resistance, it is difficult to detect gas molecules with low adsorption energy. Compared to these resistance-based gas sensors, ionization gas sensors based on the fingerprinting ionization characteristics of the detected gases can identify different kinds of gas molecules when the detected gas molecules are ionized. There are no limits to identify gases with low adsorption energy and poor charge transfer with the sensing materials. Detection of inert gases or gas mixtures can be easily achieved in an ionization chamber. Therefore, the effect of gas adsorption on CNT field-emission properties and CNT-enhanced ionization gas sensors has attracted a great amount of research interests.

Figure 81 shows a diagram of an ionization gas sensor with an aligned MWCNT array as the anode. It consists of an MWCNT array anode, an Al plate cathode, and a 150 μm thick glass insulator between them (Figure 81(a)). Under electric fields, individual MWCNTs create very

![Figure 80. Two-terminal NO₂ gas sensor. (a) Schematic diagram of CNTs patterned with platinum contacts. (b) Electrical resistance variation of CNT arrays at an operating temperature of 165°C and NO₂ concentration between 10 and 100 ppb. (a) Reprinted from Diamond and Related Materials, 17, T. Ueda et al., pp. 1586–1589. Copyright (2008), with permission from Elsevier. (b) Reprinted from Diamond and Related Materials, 13, L. Valentini et al., pp. 1301–1305. Copyright (2004), with permission from Elsevier.](image-url)
high nonlinear electric fields near the CNT tips, resulting in the formation of highly ionized gases that surrounds the MWCNT tips and the formation of a self-sustaining interelectrode discharge at very low voltages.

The precise breakdown voltage provides a finger-print to each gas and indicates the potential for gas identification within a mixture of gases. The breakdown voltage is rarely affected by the concentration in the range of $10^{-5} - 10^{-1}$ mol/l, while the breakdown voltage of each gas is unique (Figure 82(a)). Therefore by monitoring the breakdown voltage of the gas, its identity can be determined. The discharge current of each gas increases logarithmically with the gas concentration. Therefore, the discharge current provides a convenient means to quantify the concentration of the gas being detected (Figure 82(b)).

The ionization sensor works in the concentration range of $10^{-5} - 10^{-1}$ mol/l. In the lower concentration, the breakdown voltage decreases with air or the argon pressure below $10^{-5}$ mol/l.
and varies slightly with the pressure above $10^{-5}$ mol/l [473]. Besides ammonia, argon and helium gases can also be detected using the ionization gas sensors.

NH$_3$ is also measured from the electrical resistance variation of CNT arrays using two-terminal CNT sensors [472,475]. NH$_3$ exposure increases the electrical resistance of p-type CNT arrays.

4.3.3.5 Other gas sensors Besides the exposure of the above gases, H$_2$O, C$_2$H$_6$, and ethanol exposures also increase the electrical resistance of a CNT array and can be determined by two-terminal sensors [472]. After being coated with conducting polymers such as polyvinyl acetate, the vertically aligned CNT arrays can also be used to detect cyclohexane and ethanol from electrical resistance variations [476].

4.3.4 Biosensors CNTs can be functionalized with different biomolecules such as DNA and protein [444,448,477,478]. It was found that the electronic transport and thermopower of CNTs are very sensitive to substances that affect the amount of injected charge [22,303]. Based on these unique properties including the high electron transfer rate [448] and the high electrocatalytic activity [479,480], several research groups have demonstrated that bundles of CNTs [443,444], CNT membranes [481], polymer–CNT composites [434,479,482,483], and CNT-modified electrodes [445,478,484] can be used as effective electrochemical biosensors. The main advantages of CNTs are the nanosize of the CNT-sensing element and the corresponding small amount of materials required for detectable response. The well-aligned CNT arrays have been employed to work as ribonucleic acid (RNA) sensors [431], enzymes sensors [449], DNA sensors, and even protein sensors. The biological applications of aligned CNT arrays are reviewed recently [485–487]. Here we focus on the structure properties of these CNT array biosensors and their working mechanisms.

4.3.4.1 Glucose sensors Because of the high demand for blood glucose monitoring, significant research and development efforts have been devoted to producing reliable glucose sensors for in vitro or in vivo applications. The measurement principle of oxidase-based amperometric biosensors previously relied on the immobilization of oxidase enzymes on the surface of various electrodes and the detection of the current associated with the redox product in the biological reaction. To increase the selectivity and sensitivity of amperometric biosensors, artificial mediators and permselective coatings are often used in the biosensor fabrication. Artificial mediators are used to shuttle electrons between the enzyme and the electrode to allow operation at low potentials. This approach can minimize interferences with coexisting electro-active species, but the stability and the toxicity of some mediators limit their in vivo applications. Permselective membranes are also used to eliminate interferences.

A mediator- and membrane-free biosensor was invented using CNT arrays [434]. The innovative method provides a means for measuring the cathodic current of enzymatically liberated hydrogen peroxide in metal-dispersed carbon paste biosensors. The idea of the mediator- and membrane-free biosensor is based on the reduction of hydrogen peroxide [488,489], the strong electrocatalytic effect, and a high electron-transfer rate of CNTs [436]. The technique provided a new approach for biosensor development [488,489].

The glucose sensors are also based on the CNT nanoelectrode arrays with low site densities. The aligned CNT arrays are first fabricated as the starting building block (Figure 83(a)). The detailed fabrication procedure of the CNT nanoelectrode arrays is described in Section 4.3.1. The CNT nanoelectrode arrays are pre-treated for functionalization in 1.0 M NaOH at 1.5 V for 90 s. After the electrochemical treatment, some functional groups (e.g., carboxylic acid) are created at the CNT tips (Figure 83(b)). Then enzymes are attached to the broken tips of the polished CNT arrays
using standard water-soluble coupling agents 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) and N-hydroxy-sulfo-succinimide (sulfo-NHS) by forming amide linkages between their amine residues and carboxylic acid groups on the CNT tips [434,436] (Figure 83(c)). In a typical procedure, the activated CNT nanoelectrode arrays are then immersed in a freshly prepared 10 ml aqueous solution of EDC (10 mg/ml). With stirring, 300 mg of sulfo-NHS is added to the solution. The pH of the solution is adjusted to 7. The reaction is allowed to occur at room temperature for 2 h. Then the nanoelectrode is washed quickly with cold water and immediately immersed into a degassed solution (10 ml) with the desired amount of glucose oxidase (GOx) (2 mg/ml) in a 0.1 M phosphate buffer solution (pH 7.4) with stirring. The resultant nanoelectrode array biosensor is stored at 4°C before use.

The amperometric experiment was performed in a standard single-compartment electrochemical cell that contained a nanoelectrode array electrode, a Ag/AgCl reference electrode, and a platinum wire auxiliary electrode. The electrochemical detector is connected to a portable computer. The amperometric response of the glucose biosensor based on CNT nanoelectrode arrays to glucose was recorded under steady-state conditions in a 0.1 M phosphate buffer (pH 7.4) by applying a desired potential (for interference experiments, +0.4 and −0.2 V; for the calibration experiment, −0.2 V) to the biosensor. The background response of the biosensor is allowed to decay to a steady state with stirring. When the background current becomes stable, a solution of glucose is injected into the electrolytic cell, and its response is measured and recorded.

The amperometric responses at the nanoelectrode array glucose biosensors for each successive addition of $2 \times 10^{-3}$ M glucose are presented in Figure 84. The inset is the calibration curve. Well-defined current responses for glucose were obtained by the nanoelectrode array biosensor. The reaction occurring at the biosensor is very fast in reaching a dynamic equilibrium upon each
addition of the sample solution, generating a steady-state current signal within 20–30 s. The linear response of the glucose biosensor to glucose is up to about 30 mM of glucose, which is higher than the 15 mM required for practical uses in the detection of blood glucose. The signal response curve is effective at low detection limits for glucose because of favorable signal-to-noise ratio characteristics at $-0.2 \text{ V}$. The limit of detection, based on a signal-to-noise ratio of 3, is 0.08 mM.

Besides the detection of glucose, such CNT nanoelectrode biosensors can also be used to detect ascorbic acid, uric acid, and acetaminophen. The selectivity advantage accrued from the hydrodynamic voltammograms is demonstrated in Figure 85 which compares amperometric responses for relevant physiological levels of glucose, ascorbic acid, acetaminophen, and uric acid at the GO$_x$-modified nanoelectrode array at potentials of $+0.4$ and $-0.2 \text{ V}$, respectively. Amperometric responses are obtained by a batch addition of interfering species (0.5 mM ascorbic acid, 0.5 mM uric acid, and 0.5 mM acetaminophen) after the 5 mM glucose addition at two different potentials ($+0.40$ and $-0.2 \text{ V}$). Well-defined cathodic and anodic glucose responses are obtained by the nanoelectrode array biosensor at potentials of $+0.4$ and $-0.2 \text{ V}$. At an operating potential of $+0.40 \text{ V}$, the glucose response is overlapped by large anodic contributions from ascorbic acid, uric acid, and acetaminophen. The use of a lower operating potential greatly reduces these contributions. No interference is observed at a potential of $-0.20 \text{ V}$ for the interference species, indicating high selectivity toward the glucose substrate. Such a highly selective response to glucose is obtained by the nanoelectrode array biosensor without the use of mediators and permselective membranes [434].

Cyclic voltammetric experiments indicate that the oxidation of the interfering species at the nanoelectrode array starts at about $+0.20 \text{ V}$ (ascorbic acid) and $+0.30 \text{ V}$ (acetaminophen, uric acid) with no reduction until $-0.2 \text{ V}$ [434].

4.3.4.2 DNA sensors
Coated CNT nanoelectrode arrays have also been employed as DNA sensors [431,490,491]. Each individual CNT works as an individual nanoelectrode. The smaller radius of CNT electrodes (10–100 nm) is close to the size of DNAs and makes the CNT nanoelectrode arrays applicable to detect individual DNA.

Figure 86 shows SEM images of a DNA sensor consisting of a $3 \times 3$ array of individually addressed CNT electrodes on a Si(100) wafer covered with a 500 nm thick thermal oxide. The electrodes and contact lines are 200 nm thick Cr patterned with UV-lithography. Each electrode can
be varied from $2 \times 2$ to $200 \times 200 \mu m^2$, consisting of a vertically aligned MWCNT array grown by PECVD from 10 to 20 nm thick Ni catalyst films. Figure 86(c) and (d) shows MWCNT arrays grown on 2 $\mu$m and 200 nm diameter Ni catalytic spots prepared by UV and e-beam lithography, respectively. The spacing and spot size can be precisely controlled. The diameters of the MWCNTs are uniform over the whole chip and can be controlled between 30 and 100 nm by the PECVD growth process. The number of CNTs at each spot can be varied as well by changing the thickness of the Ni film. Single nanotubes can be grown at each catalytic spot if the catalytic spot size is reduced below 100 nm. A tetraethoxysilane CVD process is employed to encapsulate each nanotube and the substrate surface with a conformal SiO$_2$ film, resulting in a mechanically stable and well-insulated matrix, followed by chemical mechanical polishing for planarization and exposing the very ends of the CNTs. Figure 86(e) and (f) shows the embedded CNT array electrodes with different patterns after polishing. Clearly, CNTs retain their integrity and are separated from one another.

The aligned MWCNT nanoelectrodes shown in Figure 86 can detect DNA at a sensitivity limit lower than a few attomoles of oligonucleotide targets. The sensitivity can be further improved to detect only thousands of target DNAs after optimization, which could provide faster, cheaper, and
simpler solutions for molecular diagnosis particularly for early cancer detection, point-of care, and field uses.

4.3.4.3 Protein sensors  Figure 87 shows the fabrication of a protein sensor from CNT arrays by nanoimprint. The supporting polymer (SU8-2002) is spin-coated onto a glass substrate containing nanotube arrays. The template protein is initially incorporated into the nanocoating and, upon
Figure 87. Fabrication of a protein nanosensor. (a) Schematic of nanosensor fabrication and template protein detection. Template proteins trapped in the polyphenol (PPn) coating are removed to reveal the surface imprints. Inset: hypothetical sensor impedance responses at critical stages of fabrication and detection. (b) Scanning electron microscopy image of a polished nanotube array after PPn coating. Inset: cross-section of a nanotube tip after polishing. (c) TEM images of a PPn-coated nanotube tip without (top) and with (bottom) hFtn. Reprinted by permission from Macmillan Publishers Ltd: Nature Nanotechnology [492], copyright (2010).

extraction of protein from the accessible surfaces on the nanocoating, the electrical impedance of the CNT array is found to be greatly reduced due to electrical leakage through the surface imprints in the nanocoating. Subsequent recognition of the template protein is detected as an increase in impedance due to the relatively lower conductivity of the protein. A critical component for the assembly of the sensor architecture is comprised of electropolymerizing non-conductive polyphenol (PPn) nanocoating onto the tips of nanotubes. Such DNA sensors can selectively recognize human papillomavirus E7 protein and is also useful for the detection of other pathogens and toxins, for diagnosing human diseases (through the detection of disease biomarkers), and for a host of proteomic applications.

In contrast to conventional protein sensors, a key architectural improvement of the CNT array sensors is the non-conductive PPn nanocoating on the nanotube tips. The level of detection (e.g., 10 pg/l was achieved for hFtn [492]) surpasses that affordable by conventional sensors by a few orders of magnitude.

4.3.5. **Catalyst**

Besides the above applications of CNT nanoelectrode arrays, other important applications exist such as catalysis. CNTs have high electron transfer rates [448] and high electrocatalytic activities [479,480]. So, CNT nanoelectrodes also have a strong catalytic effect on the reduction of hydrogen peroxide [434].
Thermal devices: thermal interface materials

Thermal interface materials (TIMs) play a key role in the heat dissipation at all levels within a microelectronic device, such as integrated chips (ICs). TIMs fill the microscopic gaps between two contacting materials to enhance the heat conduction through the interfaces. The heat from the ICs can be efficiently transferred to the heat sinks or ambient environment.

The total thermal resistance $R_{\text{TIM}}$ of real TIMs can be expressed as 

$$R_{\text{TIM}} = \frac{\text{BLT}}{k_{\text{TIM}}} + R_{c1} + R_{c2}, \quad (5)$$

where $R_{c1}$ and $R_{c2}$ represent the contact thermal resistances of a TIM with the two bounding surfaces at the interfaces, BLT the bond line thickness of the TIM, and $k_{\text{TIM}}$ the thermal conductivity of the TIM.

CNTs have high thermal conductivities. The measured room-temperature thermal conductivity for an individual MWCNT (> 3000 W/m/K) is greater than that of natural diamond and the basal plane of graphite (both 2000 W/m/K) [494]. So CNTs are considered as one of the most promising TIMs due to their high thermal conductivities.

CNTs are first used as a novel type of highly thermally conductive filler to modify micro- and nano-scale structures of the TIM materials to improve their thermal performance. After CNTs are randomly dispersed in conventional TIMs or liquids, the thermal conductivity of the composites is enhanced [333,495–497]. It is reported that the thermal conductivity is doubled with 1 wt% SWCNTs loading [495]. Some literatures reviewed the composites with random CNTs [342]. However, the thermal conductivity of the CNT composite is much lower than the value estimated from the intrinsic thermal conductivity of the CNTs and their volume fraction [498]. If all the CNTs are vertically aligned well on the substrate, phonons propagate easily along the CNTs and the arrays are able to transport heat in one direction, along the alignment of the CNTs. Aligned CNT-based interfaces should conduct more heat than conventional thermal interface materials at the same temperatures.

The distribution and alignment of the thermally conductive CNT fillers are important factors to affect the phonon transport (Figure 88). The composite with aligned CNTs shows an enhancement of 0.65 W/m/K with a 0.3 wt% loading. Comparably, the enhanced thermal conductivity of the randomly dispersed CNT composite is below 0.05 W/m/K at the same loading of 0.3 wt%. Experiments indicate that the conductivity enhancement with aligned CNTs is at least two times that without CNTs (inset in Figure 88). So the vertically aligned CNT arrays are good candidates for TIM. At the same time, the CNT arrays have very low densities, 20 times lower than that of a similar copper structure with similar cooling properties. So recently various SWCNT and MWCNT array thermal interface materials have been fabricated using thermal CVD and PECVD methods [480–495].

Besides being used as fillers in the conventional TIMs, CNT arrays can also be used directly as TIMs [500] after growth. Compared with the conventional TIMs, the thermal resistances of the pure CNT arrays are lower (Figure 89). In order to increase the thermal conductivity of CNT TIMs, the CNTs are usually fabricated by the thermal CVD method with the crowding effect (see Section 2.1.1).

In order to enhance the thermal conductivity further and enforce the mechanical strength, the conventional TIMs can be filled into the gaps between CNTs. So-prepared CNT array composites have lower thermal resistances.

Despite the massive research efforts, the CNT TIMs are not commercialized yet. The performance of most of these novel TIMs is still not high enough to overtake the current high-end...
commercial products. Many of them even generate undesirable results when compared to commercial materials. Several technical barriers have to be solved before commercial applications. Firstly, the measured highest thermal conductivity of CNT TIMs is much lower than the highest value of individual CNTs of perfect atomic structures. Secondly, the contact thermal resistances between CNTs and other substances, e.g., the polymer matrix in composites and the substrates above or below the aligned CNT arrays, are very high and cause the low overall performance of the CNT TIMs. Another main technical barrier is the significant difficulty in achieving high

Figure 88. The enhanced values of thermal conductivity versus weight fraction of CNTs. The inset is a comparison of measured thermal conductivity values of different samples. 706: Silicone elastomer 706; S160: silicone elastomer Sylgard 160. Both are thermally conductive TIMs. The CNTs are aligned under magnetic fields. Reprinted figure with permission from H. Huang et al., Advanced Materials, 17, 2005, pp. 1652–1656 [499]. Copyright John Wiley and Sons.

filling ratio and better alignment of CNTs in the TIMs. In the case of aligned CNT arrays, the gaps between the CNTs in the arrays are indeed quite large compared to their diameters, causing a rather low effective filling factor.

4.5. Electrical interconnects and vias

Semiconductor technologies with feature sizes of several tens of nanometers are currently in development and the future nanometer-scale circuits will contain more than a billion transistors in 1 cm² area and operate at clock speeds well over 10 GHz. The performance of a high-speed chip is highly dependent on interconnects/vias/contacts, which connect different microcells within a chip. The interconnects, categorized as local, semiglobal, and global interconnects depending on their length, distribute power and signal across the chips. With the rapid down-scaling of feature sizes to deep submicron levels and the increase in the integration density of the complementary metal-oxide semiconductors and frequency, which result in a significant increase in current density and corresponding upgraded operating temperature, the requirements of high current carrying and thermal transport abilities are the major concerns in interconnect design besides the RC delay for the interconnects/vias/contacts [503].

At present, copper is widely used in chip interconnect/vias/contacts for advanced integrated circuits while facing serious challenges because of its electromigration, skin effect, dispersion, signal degradation, power dissipation, and electromagnetic interference at high frequencies and at the submicron level. For example, the dimension of Cu interconnects has already reached the order of the electron mean free path in Cu (40 nm) at room temperature. The electrical resistivity of copper interconnects is increasing rapidly under the effects of enhanced grain boundary and surface scattering, longer interconnect length, and higher frequency operation [504]. The signal delay caused by the Cu interconnects becomes increasingly significant compared to the delay caused by the gates and thus affecting the circuit’s reliability when the feature size is rapidly scaled down to deep submicron levels. The rising Cu electrical resistivity with decreasing size also leads to a significant rise in the metal temperature due to self-heating (metal interconnect temperatures are above the typical device operating temperature of 100 °C [505]) leading to electromigration problems which degrade the IC performance.

The excellent electrical conductivity, high thermal conductivity, and good mechanical characteristics make CNTs a very promising candidate for interconnect applications. CNTs can conduct high current densities up to 10⁹ A/cm² [506–510], 1000 times higher than Cu. Metallic CNTs have a long electron mean free path of several microns [511] and exhibit ballistic transport properties [512]. Additionally, the excellent thermal conductivity of CNTs (5800 W/m/K [511] or 3500 W/m/K [98] while only 385 W/m/K for Cu) can remove the heat sufficiently from the chips. Significant research efforts are therefore underway to develop CNT interconnect technologies. The semiglobal and global CNT interconnects are reviewed [513] and the physical properties of SWCNT interconnects are analyzed [514] recently.

The current state-of-the-art on-chip integration of CNTs focuses on the hybrid Cu interconnect/MWCNT via systems [515–518]. The first reason is that the vias carry the highest current density among interconnects, vias, and contacts. The second is that there is no convincing method to grow dense CNT bundles of varying lengths for interconnects that are parallel to the chip surface in two perpendicular directions [519] although horizontally aligned CNTs have been grown using gas-flow methods [199,520], electric field methods [159,161,162,167,205], fluidic assembly methods [521], or template selectivity growth methods [522]. The third is that MWCNTs show metallic behaviors while it is very challenging to grow dense bundles of metallic SWCNTs because of the lack of control on SWCNT chirality to ensure metallic properties. So, most present researches have focused on the hybrid Cu-interconnect/MWCNT-via systems.
Figure 90 shows the hybrid CNT interconnect/CNT via system. Each CNT bundle consists of many individual CNTs and conducts current in a parallel manner. The CNT bundles are ideal electrical conductors when thousands of individual CNTs are tightly packed. Aligned CNT bundles can be manufactured by an in situ patterned growth of CNTs on a patterned substrate surface [516–518,523–525] or by an ex situ transfer process of the CNT forests to foreign substrates [526]. In order to grow CNT bundles on Si ICs, it is necessary to grow CNTs below the microelectronics-compatible temperatures of 400–600 °C [523]. The hot-filament CVD method discussed in Sections 1.4.3 and 3, is a suitable way to grow CNT bundles. CNT bundles are first grown from catalyst particles in the vias, aligning perpendicularly to the silicon wafer surface. Subsequently, SiO2 is deposited and the wafer is polished to open the nanotube ends for contacts.

CNT-based vias potentially offer significant advantages: longer mean free path of electrons, higher current densities, and higher thermal conductivities over copper [514].

Electrical resistance of CNT vias. When an isolated CNT is shorter than its mean free path of electrons, its resistance during ballistic transport is independent of length [509,527]. For longer isolated CNTs, the electrical resistance increases with length because of electron scattering. The experimentally measured resistance of an isolated CNT is usually much higher than the calculated resistance because of the presence of imperfect metal–CNT contacts, which gives rise to an additional contact resistance. The total resistance of a CNT via is a sum of the resistances: ballistic or scattering resistance and the imperfect contact resistance, typically in the range of 7 kΩ [528] to 100 kΩ [529] for an isolated CNT via. Such resistance is too high for actual via applications. Hence, a bundle or rope of CNTs is employed as an effective via to lower the resistance [516]. The effective resistance of a CNT bundle is

\[ R_{\text{bundle}} = \frac{R_{\text{CNT}}}{n_{\text{CNT}}} \]

where \( R_{\text{CNT}} \) is the electrical resistance of a CNT and \( n_{\text{CNT}} \) the total number of CNTs in a via if it is assumed that all CNTs are metallic and conducting. The total resistance of an MWCNT via consisting of 1000 MWCNTs can be decreased by three orders of magnitude from that of an isolated CNT, down to 100 Ω [530]. The resistance can be reduced further by increasing the CNT density in the via holes. The total resistance has been lowered to 0.59 Ω for 2 μm diameter vias with a CNT site density of 10^{11} cm^-2 [523] and 0.7 Ω for a 2 μm diameter via consisting of about 1000 MWCNTs [524] when a TiN
layer is employed in the metal–CNT contacts. Theoretical calculation indicates that the resistance of packed CNT array vias (assuming perfect contacts) formed from SWCNTs shows an improved resistance compared to Cu vias for 22–45 nm node technology or much lower than that of a Cu via of identical dimensions [514].

Current density. At the same time, preliminary experimental researches show that an array of CNT vias can carry more than an order of magnitude higher current densities than conventional copper vias [516].

Temperature. CNTs can sufficiently remove heat from the chips due to their excellent thermal conductivity [494]. Figure 91 compares the temperature rises of Cu interconnects/Cu vias with Cu interconnects/CNT vias. The temperature of the chips rises to 428 K when CNT vias are employed while up to 770 K in traditional Cu interconnects/Cu vias. The vias composed of MWCNT bundles serve as more effective heat conductors than Cu vias and can potentially reduce the temperature gradient at the backend. Because the typical via height is smaller than 300 nm, shorter than both the electron and phonon mean free paths of CNTs, CNT vias operate in both the electrical and thermal ballistic transport regimes. When CNT bundles are used only as vias integrated with Cu interconnects, the maximum interconnect temperature rise is much smaller [514]. The lower interconnect temperatures in hybrid CNT/Cu structures can lead to two orders of magnitude improvement in the mean-time-to-failure of Cu global interconnects [514]. The Cu wire delay is also improved by 30% [514].

5. Potential applications of CNT arrays

Besides the above applications described in Section 4, there are additional potential applications of CNT arrays which are relatively further away from commercialization and major progresses are still needed. We review these applications altogether in this section.

5.1. Mechanical devices

CNTs possess extremely high tensile strengths. The yield strength of SWCNTs exceeds 45 GPa [531] with an average strength of 30 GPa [95], over 20 times the yield strength of typical high-strength steels. The highest tensile strength of an individual MWCNT has been recorded to be 63 GPa. The measured Young’s modulus of SWCNTs is over 1 TPa [95,532], lower than that of MWCNTs (1.3 TPa [533] or 1.8 TPa [534]). The strain at tensile failure has been measured to be as high as 5.3% for SWCNTs [95] and 12% for MWCNTs [535]. The theoretical yield strain is up
to 9% or higher [536,537] for defect-free SWCNTs. The unique strength and flexibility of CNTs make them potentially useful in many mechanical applications, ranging from everyday items such as clothes and sport gears to fictional combat jackets and space elevators. The aligned CNT ropes, CNT sheets, and aligned CNT composites would preserve the superb mechanical properties of the individual CNTs.

There are two kinds of aligned CNT materials used for mechanical devices. One kind is aligned CNT composites where the CNTs are used as additive and embedded in a matrix. Such aligned CNTs are usually fabricated by *ex situ* methods discussed in Section 2.2. After CNTs are synthesized as described in Section 1.4, they are collected, purified, if needed, and mixed with polymeric, ceramic, or other materials. In order to improve the dispersion of CNTs in the processing composites, surfactants are usually used as a dispersing agent or the surfaces of CNTs are chemically functionalized. If the CNTs are randomly dispersed in the matrix, the mechanical properties of such composites are slightly enhanced. For example, random CNTs have been employed to enhance the mechanical strength of swords [10,538]. In order to align the CNTs in the matrix, force fields [117,254,539–541], magnetic fields [542,543], or electric fields [261,544–548] are applied on the liquid-like mixture. CNTs are aligned along a certain direction. The alignment methods for CNTs in matrices were reviewed [251] and discussed in Section 2.2.

The other kind is the aligned CNTs without matrices. The aligned CNTs can be synthesized first and then aligned to achieve an ordered structure, such as CNT ropes, CNT clothes, CNT films, etc. The details of the alignment methods are discussed in Section 2.2. The aligned CNTs can also be *in situ* grown directly on a substrate (see Section 2.1). Below we review the applications of both kinds of aligned CNT materials.

5.1.1. Carbon nanotube ropes

The CNT ropes are fabricated by spinning methods, including the wet-spinning and the dry-spinning methods, as described in Section 2.2.3.2. The mechanical properties of CNT ropes or bundles are reviewed recently [259]. The mechanical properties of CNT ropes are lower than those of the individual CNTs. The CNTs in ropes are aligned parallel to one another [549] or twisted [550]. In the un-twisted ropes, the CNTs are held together by van der Waals interactions and the un-twisted ropes' tensile strength is so weak that the rope breaks once pulled [550]. So the CNT ropes are usually twisted to increase the strength [550]. The twisted pure CNT ropes can be fabricated by wet-spinning from CNT solvents [263] or dry-spinning directly from CVD-grown CNTs [262,550]. The fabrication details are discussed in Section 2. Figure 92 shows MWCNT ropes prepared by the dry-spinning method from CVD-synthesized CNT forests. Its stress–strain curve is shown in Figure 93.

Detailed experimental results indicate that the CNTs in the twisted ropes are arranged in a helical structure. The mechanical properties of CNT helical ropes depend on the microstructure of the ropes. The frictional force coupling CNTs in the twisted CNT ropes affects the tensile strength of the CNT ropes. The tensile strength of twisted CNT ropes $\sigma_{\text{rope}}$, follows the mechanical properties of textile fiber yarns [550,551] and can be expressed as [552]

$$
\sigma_{\text{rope}} \approx \sigma_{\text{CNT}} \cos^2 \alpha \left[ 1 - \frac{\sqrt{dQ/\mu}}{3L} \cos \alpha \right], \quad (6)
$$

where $\sigma_{\text{CNT}}$ is the tensile strength of the CNT, $\alpha$ the helix angle that CNTs make with the rope axis, $d$ the CNT diameter, $L$ the CNT length, $Q$ the CNT migration length, and $\mu$ the friction coefficient between the CNTs. The CNTs in the twisted rope are inclined at the angle $\alpha$ with respect to the tensile axis. The tensile strength decreases with the helix angle $\alpha$ [551]. For short CNTs, however, there is little strength in the absence of twist because there are no significant transverse
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Figure 92. SEM images of polymer-free CNT ropes. (a) Single MWCNT rope. (b) Two-ply MWCNT rope. (c) Four-ply MWCNT rope. From M. Zhang et al., Science, 306, pp. 1358–1361, 2004 [549]. Reprinted with permission from AAAS.

Figure 93. Stress–strain curves of single (black), two-ply (red), and PVA-infiltrated single (blue) ropes at a strain rate of 1%/min for a centimeter gauge length. From M. Zhang et al., Science, 306, pp. 1358–1361, 2004 [549]. Reprinted with permission from AAAS.

forces to bind the CNT assembly together. The transverse forces are generated by transfer of the tensile load to the rope surface, which locks the fibers together forming a coherent structure [550]. The tensile strength of a twisted rope increases with increasing coefficient of friction between CNTs, with CNT length, and with decreasing CNT diameter and CNT migration length. The highest Young’s modulus of the helical SWCNT ropes drawn from coagulation solution (polymer is removed and CNT ropes mainly consist of CNTs) is about 15 GPa [265], with yield stress of 8.8 GPa and stiffness of 357 GPa for CNT ropes spun directly from an aerogel CNTs [553], and tensile strength of 150–300 MPa for MWCNT ropes fabricated directly from CNT forests [550]. The strength is higher than most of commercial high-performance fibers while still more than an order of magnitude lower than the intrinsic modulus of individual SWCNTs of 37 GPa.

In order to increase the friction between CNTs, CNTs can be embedded in a polymer with high strength and high-modulus like polyvinyl alcohol (PVA). The CNT/polymer ropes can be fabricated by wet-spinning or dry-spinning followed by soaking in a polymer solution. The tensile strength of SWCNT/PVA yarns increases to 850 MPa from 150 to 300 MPa of PVA-free yarns. The strength is still much lower than that of individual SWCNTs. Creep is a major problem for these CNT composite ropes.
Twisted polymer fibers consisting of CNTs at less than 10 wt% have also been fabricated. The mechanical strength and modulus are enhanced compared with pure polymer fibers [539]. It is reported that the tensile strength and Young’s modulus have reached 4.2 and 167 GPa, respectively, in the dry-jet wet spinning poly(p-phenylene benzobisoxazole)/SWCNT ropes (SWCNT: 10 wt%) [554]. When the SWCNTs are lower than 2.1 wt%, the additive of SWCNTs does not enhance the mechanical properties [555].

In order to avoid creeping, two-ply ropes are fabricated by over-twisting a single rope (Figure 92(b)), and four-ply ropes by oppositely twisting a two-ply rope (Figure 92(c)), and even knitted or knotted ropes are fabricated. Higher tensile strength values of 250–460 MPa are measured for two-ply yarns, while only 150–300 MPa for single-ply yarns (Figure 93).

Figure 94 shows Young’s modulus of CNT ropes with different diameters. Both experimental data [556] and theoretical analysis [557] indicate that the tensile modulus depends strongly on the diameter of the CNT ropes because of the creeping between CNTs. With the increase in rope diameters, Young’s modulus is diminished by approximately 68% when upscaling from nanoscale to microscale.

5.1.2. **TEM grids**

The continuous CNT sheets with centimeters in width and tens of nanometers in thickness can be fabricated by spinning methods [262,549,558] as described in Section 2.2.3.2. The CNTs are parallel-aligned in the drawing direction and end-to-end jointed to form a continuous thin film, having a much better alignment than the as-synthesized CNT arrays [558]. These aligned CNT sheets are transparent and highly conductive [264,558,559], as a good candidate for TEM grid supporting films.

Figure 95 shows the morphologies of a TEM grid. In the fabrication of TEM grids, four layers of CNT thin sheets are directly cross-stacked layer by layer on TEM copper grids, then an organic solvent is dispensed on the sheets to bond the sheets onto the copper grid, following a CNT sheet cutting by a focused laser beam. The ultrathin CNT sheets cover the copper grid base and regular networks with numerous holes are formed. The holes are mostly less than 1 μm in diameter, and the nanometer-sized holes are more than 60% of all holes. Considering the good electrical conductivity and mechanical strength of CNTs, these TEM grids are ideal tools for the characterization of nanomaterials. HRTEM image of nanoparticles (Figure 95(c)) shows a clear...
profile and the fine structures of an individual nanoparticle attached to a CNT of the TEM grids covered with CNT sheets.

In comparison with conventional TEM holey carbon grids, the TEM grids with CNT sheets have some advanced characteristics resulting from the excellent intrinsic physical properties of CNTs [560]. Firstly, the CNT has strong adsorbability— it can easily adsorb small nanoparticles and ensure them to be suspended stably during TEM observation. Secondly, due to good conductivity of MWCNTs, the CNT sheet also has good electrical conductivity (bulk resistivity is about $3.8 \times 10^{-4}$ Ω m). Thirdly, because of the fixed interspace between sidewalls of the MWCNTs, i.e., $\sim 0.34$ nm, the CNT grid can be a standard sample for calibration of HRTEM magnification and size measurement of specimens. In addition, the CNT sheet has a better thermal stability than that of the conventional amorphous carbon film.

5.1.3. Mechanical tapes

Replicating the multiscale structure of micron-size setae and nanometer-size spatulas of gecko lizard feet using microfabricated MWCNTs, CNT arrays can translate weak van der Waals interactions into enormous attractive forces [561]. The CNT block arrays (50–500 μm patches) are synthesized from photolithographic patterns as described in Section 2.1.3. Each block array works as micron-size setae and consists of thousands of individual MWCNTs, the nano-sized spatulas. These patterned CNT arrays can stick to both hydrophobic and hydrophilic surfaces with a maximum shear stress of 36 N/cm², nearly four times higher than the gecko foot and 10 times higher than polymer pillars. The shear forces supported by the patterned CNT arrays are very stable and time-independent.

5.2. Electrical devices

SWCNTs are metallic or semiconducting according to their structures. The electronic properties of perfect MWCNTs are rather similar to those of perfect SWCNTs. In the 1D electronic structure, electrons transport in metallic SWCNTs and MWCNTs over long nanotube lengths, carrying high current densities [304]. So much research work has been carried out to add random CNTs into various composites to enhance electrical conductivity. Depending on the composite matrix, conductivities of 0.01–10 S/m can be obtained for 5 wt% MWCNT loading or 0.1–0.2 wt% SWCNT loading in polymers. Such high conductivities and dissipate electrostatic charges [318,495], having
potential applications in electrostatic discharge and electromagnetic radio interference protection. The preparation and electrical properties of random CNT composites are reviewed [340]. The electrical conductivity of CNT composites also depends on the alignment as well as the concentration of CNTs [562,563]. Here we review several electrical applications of aligned CNTs without matrices.

5.2.1. Low $\kappa$ dielectrics

Electrically insulating layers are required in integrated circuits on semiconductor substrates to reduce the coupling capacitance of interconnects. The low $\kappa$ materials with low relative dielectric constants are employed as the insulating layers in integrated circuits to reduce the coupling capacitance. Amorphous silicon dioxide with or without fluorine, hydrogen, or alkyl groups is often used as the dielectric to electrically insulate the metallic interconnects from one another. The relative dielectric constant of electrically insulating layers can be reduced further by introducing cavities into the low-$\kappa$ materials. The $\kappa$-value decreases linearly with the cavity volume fraction. The simulation calculations demonstrate that the effective $\kappa$ value is also affected by the morphology of the cavities. If elongated and oriented pores are used, it is possible to reduce significantly the effective $\kappa$ value without increasing the proportion of the cavity volume in a dielectric. With the same proportion of cavity volume, a reduction of 13% is achieved with a cavity aspect ratio of 4:1 and a reduction of 20% is achieved with a cavity aspect ratio of 24:1 when the cavities are oriented perpendicularly to an electric field.

CNTs have a high aspect ratio and can be used to introduce elongated, oriented pores into a low-$\kappa$ dielectric to further reduce the effective $\kappa$ value of the dielectric.

In a typical procedure, aligned CNT forests are grown on a desired surface using PECVD methods as described in Section 2.1.3. Silicon dioxide is deposited between and on top of CNTs. The oxide is removed by mechanical polishing or by a dry-etch process to expose the CNTs. In order to create the oriented pores in the oxide, the CNTs are subsequently removed by high-temperature oxidation and/or oxygen or hydrogen plasma.

5.2.2. Random access memory

Aligned CNTs can serve as addressable electromechanical switches arrayed across the surface of a microchip, storing hundreds of gigabits of information (Figure 96). When an electric field is applied to a nanotube, the electric field causes the CNT flex downward into a depression onto the chip’s surface, where it contacts metal electrodes (in another design, the CNTs touch other nanotubes [564]). Once bent, the nanotubes maintain their shapes, including when the power is turned off, allowing for a nonvolatile operation. Van der Waals forces hold the switch in place until application of a field of different polarity causes the nanotubes to return to their straightened positions. The binary 0 state corresponds to the nanotubes suspended and not making contact with the electrode (Figure 96(b)). When a transistor turns on, the electrode produces an electric field that causes the aligned CNTs to bend and touch an electrode, a configuration that denotes a 1 state (Figure 96(c)).

5.2.3. Transistors

Figure 97 shows a transistor array made from vertically aligned CNTs grown on a template of porous aluminum oxide as described in Section 2.1.3.2. In the integrated device, each CNT is electrically attached to a source electrode (lower electrode in Figure 97(b)) and a drain electrode (upper electrode in Figure 97(b)). The gate electrode is located close to the nanotubes. Current
flows from the source electrode to the drain electrode and can be switched on or off by applying a voltage to the gate. Figure 97(c) shows a current–voltage curve of a CNT transistor.

5.3. **Thermoacoustic loudspeakers**

The thermoacoustic phenomenon was discovered in the late nineteenth century. When an alternating current passes through a thin conducting plate or wire, a periodic heating takes place in the conductor because of Joule's effect, following the periodic change of the current amplitude. This periodic heating causes a periodic temperature oscillation that heats the surrounding medium (usually air) near the conductor surface, resulting in the contraction and expansion of molecules near the conductor while the conductor remains static. The vibrating movement of the molecules results in the generation of an acoustic wave. In a conventional thermoacoustic device (thermophone), the acoustic element is a thin metal film such as a gold film with a thickness of 285 nm [567] and a platinum strip with a thickness of 1.8 μm [568].
To obtain appreciable amplitudes of acoustic waves, it is essential that the conductor be very thin and its heat capacity be very low to conduct the produced heat at a high rate [568]. CNTs have an extremely low heat capacity and good thermal conductivity, CNT sheets can be heated up to 2000 °C in less than 1 ms, and the sheet temperature synchronizes with electrical currents in a wide frequency range of 1–10^5 Hz [403]. The thickness of CNT sheets is also very small, less than microns. So CNT sheets are one of the best candidates for thermoacoustic devices.

Figure 98(a) shows a CNT sheet loudspeaker. The CNT sheets are directly drawn out from CNT forests consisting of superaligned CNTs with diameters of 10 nm. Such a dry-spinning method is described in Section 2.2.3.2. The thickness of the CNT sheet is of tens of nanometers. The CNT sheet loudspeaker is formed by directly putting the CNT sheet on two electrodes. When a sinusoidal voltage is applied across the two electrodes, clear and loud tones are emitted from the CNT sheet.

Figure 98(b) shows the input voltage and the output sound pressure. The output sound pressure is measured by a microphone near the CNT sheet. It is noted that the frequency of the sound pressure doubles that of the input voltage, as observed in a conventional thermophone. When an alternating current passes through the CNT sheet, the CNT sheet is heated twice, once during positive and once during negative half-cycles of the alternating current, resulting in a double-frequency temperature oscillation, as well as a double frequency sound pressure [569]. The output sound with doubled frequency always sounds strange. In order to reproduce human voice and music with normal frequency without introducing the double frequency effect, a direct current bias must be superimposed to the alternating current. When the strength of the direct current is several times higher than that of the alternating current, the double frequency effect can be negligible [568]. Then the CNT sheet loudspeaker can possess all the functions of a voice-coil loudspeaker (Figure 98(b)) [569].

The CNT sheet loudspeaker can generate sound in a wide frequency range (1–10^5 Hz). The high sound pressure level increases with increasing frequency and the sound pressure is proportional to the input power. The sound pressure produced by the CNT sheet under an alternating current can be expressed as [568]

\[
P_{\text{rms}} = \left( \frac{\sqrt{\alpha} \rho_0}{2\sqrt{\pi} T_0} \frac{\sqrt{f}}{C_s} \right) P_{\text{input}} \frac{r}{r} \quad (7)
\]

in an open system (a more accurate while more complex expression is derived in references [569,570]), in which \( C_s \) is the heat capacity per unit area of the CNT sheet, \( f \) the frequency of

![Figure 98. Thermoacoustic CNT loudspeaker. (a) Optical image of a thermoacoustic CNT sheet loudspeaker. (b) Real-time signals of the input voltage of a CNT thin-film loudspeaker and the output sound pressure from the microphone, indicating that the frequency of the sound pressure doubles that of the input voltage. The phase shift between the input voltage and the output sound pressure signal is primarily due to the sound propagation from the CNT sheet to the microphone detector. Reprinted with permission from L. Xiao et al., Nano Letters, 8, 2008, pp. 4539–4545 [569]. Copyright (2008) American Chemical Society.](image-url)
sound, \( P_{\text{input}} = I^2 R \) the input electrical power proportional to the square of applied root-mean-square (rms) current \( I = I_0 \sin(\omega t) \), \( R \) the resistance of the CNT sheet, \( r \) the distance between the thin CNT sheet conductor and the sound pressure detector (microphone), \( \rho_0, T_0, \) and \( \alpha \) the density, average temperature, and thermal diffusivity of the surrounding medium, respectively, and \( P_{\text{rms}} \) the root-mean-square sound pressure.

Equation (7) indicates that the produced sound pressure decreases rapidly with distance. Usually the temperature of the CNT sheet is also a sinusoid of time, and the temperature waves propagate into the atmosphere on either side. The periodic temperature change in the thin boundary layer near the CNT sheets account for the sound vibration. Calculation shows that the temperature waves propagate into the working medium and are practically extinguished after one wavelength (27 \( \mu \)m in air and 2.0 \( \mu \)m in water) has been traversed [568].

According to Equation (7), the sound pressure generated by CNT sheet loudspeaker is 260 times higher than that generated by a conventional thermophone with a 700 nm thick Pt film as the acoustic element, corresponding to a 48 dB difference in the sound pressure level [569]. The measured sound pressure level of the CNT loudspeaker is over 100 dB at high frequencies, higher than the conventional thermoacoustic device with a gold film of 285 nm in thickness as the acoustic element (63 dB) [567].

The pressure generation efficiency coefficient \( \xi = \left( \frac{\sqrt{\alpha \rho_0}}{2 \sqrt{\pi T_0}} \right) \left( \frac{f}{C_s} \right) \) is affected by many parameters [571], such as (1) the ability of the CNT sheet to be rapidly electrically heated and then to transfer heat to the surrounding medium at high rates, thereby returning to a starting temperature within the excitation cycle; (2) the working medium, which enables rapid heat transfer while minimizing effective increase in the heat capacity of the projector material, and surviving the possible extreme temperature of the CNT sheets; and (3) possible packaging, which provides protection for the CNT sheets and efficient transmission of internal acoustic oscillation to external locations. Theoretical calculation indicates that a CNT sheet working in argon has a higher generation coefficient than that in air or in helium while 100 times higher than that working in liquids, such as water, methanol, and ethanol [571].

Besides the freestanding CNT sheet loudspeaker, CNT sheets are also encapsulated into an argon- or air-filled chamber. Such encapsulated CNT loudspeakers can be used in liquids, such as water [571]. In the small enclosure, the sound pressure is \( P_{\text{rms}} = \left( \frac{\sqrt{\alpha \rho_0 T_{\text{surf}}}}{4 V_0 T_{\text{ave}} C_s f^{3/2}} \right) \times P_{\text{input}}, \) where \( T_{\text{surf}} \) is the temperature of the surface of the CNT sheet, \( T_{\text{ave}} \) the average temperature of the filled gas, and \( V_0 \) the volume of the enclose [568]. The produced pressure causes a vibration of the attached enclosure windows with a resonant frequency \( f_r \) (\( f_r = 3.28 \) kHz when working in air and 1050 Hz when immersed in water [571]). The highest sound pressure level is over 130 dB, 30 dB higher than that exposed to air. The total energy conversion efficiency of the argon-encapsulated thermoacoustic device is 0.2%, while that of CNT freestanding sheet device in air does not exceed 0.001%.

### 5.4. Electrochemical/chemical storage devices

Systems for electrochemical energy storage and conversion include batteries, fuel cells, and electrochemical capacitors [572]. Although the mechanisms are different, the common features are that the energy-providing processes take place at the phase boundary of the electrode/electrolyte interface and that electron and ion transports are separated. All of them consist of two electrodes in contact with an electrolyte solution. Figure 99 is a simplified Ragone-diagram disclosing the specific power and specific energy of these three electrochemical storage systems. Fuel cells can be considered to be high-energy systems and supercapacitors to be high-power systems while batteries have intermediate power and energy characteristics. Although no single electrochemical power source can match the characteristics of the internal combustion engine (high power and high
energy), some hybrid electrochemical power sources combining fuel cells (deliver high energy) and supercapacitors (provide high power) will be competitive with regard to the combustion engines and turbines in the future.

Most favorable electrodes in these electrochemical storage systems are porous electrodes with large surface areas and low polarization. The porous structures of electrodes increase the surface area for reaction and shorten the diffusion path lengths to the reaction sites. The location of the reaction site inside a porous electrode is strongly dependent on the characteristics of the electrode structures and the reactions themselves. The key parameters include conductivity, porosity, and pore size of the electrodes besides the characteristics of the electrolyte and the reactants [572]. The effectiveness of a porous electrode can be estimated from the active surface area $S$ and the penetration depth of the reaction process into the porous electrode.

CNTs are the electrode material of choice because a CNT combines a large surface area wetted by an electrolyte, a high electrical conductivity, and a high chemical, mechanical, and electrochemical stability. The electrochemical behaviors of CNTs have been studied [422,442,443, 448,479–481,484,573,574] because of their good electrical conductivity/chemical inertness/wide potential range. Below we discuss the application of aligned CNT arrays as porous electrodes in these chemical storage devices. Because of the large electrochemically accessible surface area of CNT arrays, combined with their high electrical conductivity and useful mechanical properties, CNT arrays are attractive as electrodes for devices that use electrochemical double-layer charge injection [318].

5.4.1. Fuel cells

Fuel cells, one kind of electrochemical energy storage devices, are made up of three sandwiched segments similar to ultracapacitors and batteries: an anode, an electrolyte, and a cathode, in a reaction cell. Different from ultracapacitors and batteries in which the energy is stored in the cells and consumed, electricity is produced inside the fuel cells through the reactions between an
external fuel and an oxidant in the presence of an electrolyte. At the anode, a catalyst, usually Pt nanoparticles, oxidizes the fuel, usually hydrogen, hydrocarbons, and alcohols, turning the fuel into positively charged ions and negatively charged electrons. The electrolyte (usually composed of aqueous alkaline solution, polymer membrane, phosphoric acid, molten carbonate, and solid oxide substrates) blocks the transportation of electrons while conducting ions. On the cathode, the ions traveling through the electrolyte are re-united with the electrons passing through a load during a reaction with an oxidant, such as oxygen, chlorine, and chlorine dioxide, to produce water or carbon dioxide. In a typical fuel cell using methanol as the fuel, methanol is oxidized to produce ions and electrons at the anode in a polymer electrolyte:

$$\text{CH}_3\text{OH} + \text{H}_2\text{O} \xrightarrow{\text{catalyst}} 6\text{H}^+ + 6\text{e}^- + \text{CO}_2$$  \hspace{1cm} (8)

and oxygen combines with electrons and $\text{H}^+$ ions at the cathode catalyst surface to form water:

$$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$$  \hspace{1cm} (9)

Fuel cells can operate continuously as long as the fuels and the oxidants are well maintained [572].

Platinum and platinum alloys seem to be the best choice of catalysts for the electroreduction of oxygen in an acidic media [575]. The catalytic nanoparticles are deposited on porous materials, like activated carbon, as electrodes. The electrocatalytic activity of platinum catalyst is dependent on many factors [576]. Among them, the good properties of the catalyst supports, such as high surface area and good electrical properties, are essential for a Pt catalyst to highly promote catalytic activities [577]. The large accessible surface area, low resistance, and high stability of CNTs [578,579] suggest that CNTs are suitable materials for electrodes and catalyst supports in fuel cells. The nanoparticles with electrocatalytic activities may decorate the external walls or be encapsulated in the interior of the CNTs [104]. Several papers have studied the electrocatalytic properties of tangled and substrate-free CNTs [423,580–584]. More details of electrocatalytic activities using CNT electrodes are reviewed recently [585,586]. Pt has been deposited on activated SWCNTs or MWCNTs by chemical reduction methods and the resultant electrodes show good electrocatalytic properties for hydrogenation [580], and oxygen reduction [423,582]. Below we review the electrocatalytic properties of CNT arrays.

Figure 100 shows the electrocatalytic properties of a Pt/CNT electrode for oxygen reduction reaction investigated by linear sweep voltammetry in a 0.1 M H$_2$SO$_4$ aqueous solution. The well-aligned CNT arrays are synthesized by the PECVD method (see Section 2.1.3) on a titanium substrate as the working electrode. The CNT diameters are 50–70 nm and the lengths are 3–4 μm [578]. Experiments show that no O$_2$ reduction current is observed using CNT array electrodes or using graphite electrodes over the studied potential range [578]. This means that the CNT arrays and the graphite substrate result in no obvious electrocatalytic activities. Then Pt catalysts are deposited on the CNT arrays using a potential-step electrodeposition method. Pt catalytic nanoparticles are also deposited on a conventional graphite electrode for comparison. After Pt coating, electrocatalytic activity is observed (Figure 100). Figure 100(a) and (b) are the linear sweep voltammograms of Pt/CNT and Pt/graphite electrodes at different Pt deposition charges, respectively. For Pt/CNT electrodes, a large oxygen reduction current is observed at 0.36 V, which is the typical potential for oxygen electroreduction on platinum catalysts in a H$_2$SO$_4$ solution [587]. The specific current, defined by peak current density (mA/cm$^2$) per unit of deposition charge ($\mu$C/cm$^2$) [587], is used to evaluate the electrocatalytic activity of Pt catalysts for oxygen reduction activities. When the Pt loading mass is low (deposition charge: 9.744 $\mu$C/cm$^2$), the specific current of the Pt/CNT electrode (solid curve in Figure 100(a)) is 0.41 mA/$\mu$C, which is 1.4 times as large as that of a Pt/graphite electrode (dashed curve in Figure 100(a)). At a
Figure 100. The linear sweep voltammograms of Pt/CNT arrays in N\textsubscript{2} saturated 0.1 M H\textsubscript{2}SO\textsubscript{4} aqueous solution. For comparison, the voltammograms of platinum-electrodeposited graphite disk electrode (geometry area 1.71 cm\textsuperscript{2} prepared at the same conditions) are also plotted as dashed curves. (a) Pt nanoparticles disperse individually on CNT walls with a deposition charge of 9.744 μC/cm\textsuperscript{2}. (b) Pt nanofilm is deposited on individual CNTs with a deposition charge of 572.5 μC/cm\textsuperscript{2} while the coated CNTs huddle together to form bundles of 2–10 CNTs. Linear sweep rate is 200 mV/s. Reprinted from Carbon, 42, H. Tang \textit{et al.}, pp. 191–197 [578]. Copyright (2004), with permission from Elsevier.

high deposition charge (572.5 μC/cm\textsuperscript{2}), the specific current of the Pt/CNT electrode (solid curve in Figure 100(b)) is almost twice as large as that of a Pt/graphite electrode (dashed curve in Figure 100(b)). These results imply that the Pt/CNT electrodes possess higher electrocatalytic activities for oxygen reduction.

The increase in the O\textsubscript{2} reduction activity of Pt/CNT array electrodes may be attributed to the following two factors: (i) high dispersion of Pt nanoparticles on the 3D structure of CNT electrodes can provide large acceptable surface areas of Pt nanoparticles for oxygen reduction; (ii) the particular structure and electrical properties of CNT arrays may be beneficial to the electrocatalytic reduction of oxygen. A previous study on the dissociation of adsorptive oxygen on the surface of CNTs suggested that CNTs have the ability to promote electron-transfer reactions [574]. Additionally, the activity of the catalyst, which could be involved in the interaction between metallic catalyst and catalyst support, can be strongly affected by the properties of the supporting materials. These results imply that well-aligned CNT arrays may be a good candidate for the cathodic catalyst supports in fuel cells.
More detailed studies on the kinetics of oxygen reduction reaction at Pt/CNT electrodes indicated that the activation energy of Pt/CNT electrodes is lower than that of Pt/graphite electrodes at the same cathodic over-potential [578]. This suggests that CNTs have a beneficial effect on the kinetics of oxygen reduction.

Pt/CNT arrays can also oxidize methanol [588]. And the oxidation activity of the Pt/CNT electrodes is increased after nitrogen doping.

Besides working as novel catalyst supports (e.g. random CNTs [584,589] and CNT arrays [578]), CNT arrays with iron catalyst may highly promote electrocatalytic activity themselves after nitrogen doping and can replace Pt catalysts [479,480,590,591]. Figure 101 shows the cyclic voltammograms for CNT arrays taken in either argon- or oxygen-saturated aqueous electrolytes. CNT arrays are synthesized using ferrocene as the source of catalyst and ammonia as the nitrogen dopant. The catalytic iron nanoparticles are kept on the CNT tips and the as-synthesized CNT arrays are used as cathodes. The CNTs are doped by nitrogen from ammonia during the CNT growth. The average content of nitrogen of the nitrogen-doped CNT arrays is 3.44 at%. Compared with the un-doped CNT arrays (Figure 101(b)), the electrocatalytic activity of the nitrogen-doped CNT arrays is enhanced significantly (Figure 101(a)), as observed in random CNTs [592]. It is believed that active sites of nitrogen and iron with carbon have contributed to the oxygen reduction reaction.

Recently, it is found that the nitrogen-containing CNT arrays without metal inclusions also promote good electrocatalytic activities. Figure 102 plots the cyclic voltammogram for the oxygen reduction reaction of nitrogen-doped CNT array electrodes. The CNT arrays are free of iron catalysts and have a nitrogen content of 4–6 at%. Compared to Pt/carbon electrodes, the CNT array electrodes result in a much better electrocatalytic activity, long-term operation stability, and more tolerance to crossover effects than platinum for oxygen reduction in alkaline fuel cells. The vertically aligned CNTs reduce oxygen more effectively in alkaline solutions.

5.4.2. Supercapacitors

Supercapacitors, also termed as electric double-layer capacitors or ultracapacitors, are electrochemical capacitors that store the electrostatic charges through adsorbing electrolytic ions onto a conductive electrode material with a large accessible specific surface area. The high capacitance of supercapacitors depends on the accessible specific surface area and the double layer adsorbing ions. Supercapacitors can be fully charged or discharged in seconds and achieve a high power output (10 kW/kg) in a few seconds [593] while their energy density (~5 kWh/kg) is lower than that of batteries. Supercapacitors currently bridge the conventional electrolytic capacitors and

Figure 101. Cyclic voltammograms of (a) nitrogen-doped CNT arrays and (b) CNT arrays without nitrogen measured in a 0.6 M HCl electrolyte saturated with argon or oxygen at a scan rate of 10 mV/s. Ferrocene is used for CNT catalyst and not removed from CNTs. J. Yang et al., Chemical Communications 3, pp. 329–331, 2008 [589] – Reproduced by permission of The Royal Society of Chemistry.
traditional batteries because they combine the unique properties of conventional capacitors (high power density) and that of traditional batteries (high energy density) [594].

Supercapacitors consist of two electrodes immersed in or impregnated with an electrolyte solution with a semi-permeable membrane serving as a separator that prevents electrical contact between the two electrodes. Figure 103 schematically illustrates a supercapacitor made of CNT array electrodes. The supercapacitors store the electrostatic charges by reversible absorption of electrolytic ions on active materials with large accessible specific surface areas. Usually activated carbon and porous carbon are used as the active materials because of their large specific surface areas ($1000–3500 \text{ m}^2/\text{g}$). When an electric potential is applied to the electrodes, a potential difference is created at the electrode–electrolyte interface because of the charge separation from polarization. This electrostatic interface consists of a double-layer between the ions in the electrolyte and the electrical charges on the electrode. The capacitance of a supercapacitor is generally...
assumed to follow that of a parallel-plate capacitor based on the Helmholtz model\textsuperscript{1} [595]:

\[
C = \frac{\varepsilon_0 \varepsilon_r A}{d}, \quad (10)
\]

where $\varepsilon_r$ is the dielectric constant of the electrolyte, $\varepsilon_0$ the permittivity of vacuum, $A$ the specific surface area of the electrode accessible to the electrolyte ions, and $d$ the effective thickness of the electrical double-layer. In the supercapacitors, the electrical energy is stored as the electrostatic charges based on the separation of charged species in an electrical double-layer across the electrode–solution interfaces and there is no faradic (redox) reaction.

The active materials with high specific surface area and electrically conducting electron collectors produce high capacitances. In conventional supercapacitors, activated carbon or glassy carbon are employed as electrodes. The graphitic carbon is a good candidate for supercapacitors because of their high conductivity, high electrochemical stability, and porous structures. Up to now, the double-layer capacitance of porous carbon with a broad distribution of pore sizes reaches 100–200 F/g in organic electrolytes and exceeds 370 F/g in aqueous electrolytes [596]. The larger surface area of activated carbon promotes absorption of ions on electrodes, leading to an enhanced capacitance [597] and store more energy than the conventional capacitors.

It is observed that the capacitance of supercapacitors is maximum when the electrode size is close to the ion size [598], confirming the capacitance contribution from pores with sizes smaller than the solvated ion size. CNTs are aligned regularly, possessing regular pore structures, and adjustable pore sizes, and therefore are the best candidates for supercapacitor electrodes.

The CNT arrays have larger surface areas than activated carbon to store electron charges in supercapacitors. In addition, the CNT site density can be adjusted to store elementary charges, such as electrons, and consequently the capacitance may be increased considerably.

Supercapacitors have giant capacitances in comparison with those of ordinary dielectric-based capacitors. Like ordinary capacitors, CNT supercapacitors are typically comprised of two electrodes separated by an electrically insulating material, which is ionically conducting in electrochemical devices [599,600]. The capacitance depends on the separation between the charges on the electrodes and the countercharges in the electrolyte that contributed mostly to the capacitance. Very large capacitances result from the large CNT surface area accessible to the electrolyte. These capacitances depend on the surface area of the CNT array. The capacitances of 180 and 102 F/g are achieved for random SWCNT electrodes and MWCNT electrodes, respectively. It is typically between \sim 15 and \sim 200 F/g when random CNTs are employed [599,600]. The capacitances come from the large amounts of charge injection when only a few volts are applied. The application of CNT arrays as capacitors are reviewed recently [594,596,601,602].

The CNT array electrodes possess lower ion diffusion resistance, higher electrical conductivity, larger pores, and more regular pore structure than the electrodes consisting of random CNTs. So, the CNT array electrodes have higher capacitances, lower resistances, and better rate performances [601].

The CNT array electrodes can be fabricated \textit{ex situ} or \textit{in situ}. In \textit{ex situ} procedures, CNT arrays are grown by CVD methods described in Section 1.4. Then they are detached from the substrates, re-attached onto an electrically conductive current collector by binding [603], soldering, or surface tension, to form a CNT array electrode. The CNT array electrodes can also be fabricated from random CNTs by self-assembly processes [604]. In \textit{in situ} procedures described in Section 2.1, a CNT array can be directly grown on a current collector to form an electrode [605–607]. The procedure is a one-step process, and the electrical resistance between the CNT array and the current collector is relatively low.

CNT arrays store energy by the electrochemical double-layer formed on the surfaces of each CNT in the array. Since the capacitive properties of the array-like CNT membranes were studied...
Capacitance of 18 F/g was obtained in 6 M KOH electrolytes using a 400 μm long CNT array directly grown on a metallic alloy [606], and 35 F/g was obtained in 6 M KOH using a CNT array embedded in cellulose [608]. The cyclic voltammetry curves indicate that the contact resistance between the CNTs and the current collector is low. Beside the aqueous electrolytes, organic electrolytes are also tested. Capacitances of 22 F/g in ionic liquid electrolyte [608], 80 F/g in 1 M Et4NBF4/PC electrolyte using SWCNT arrays [609], 10–15 F/g in organic electrolytes at an extremely high current density of 200 A/g [610], 83 F/g in organic electrolytes using a DWCNT array of 300 μm in length grown on a conductive Si substrate [611], and 27 F/g in organic electrolytes [607] are reported.

Experimental results indicate that the CNT array electrodes possess lower ion diffusivity resistances and higher electrical conductivities, better rate performances, and higher capacitances than random CNTs because of the regular pore structure and the large pore size of CNT arrays.

Although CNT array electrodes possess a higher rate capability than any other electrochemical electrode materials, their capacitances are moderate, i.e., 10–80 F/g [607,611,612], lower than the activated carbon and pseudo-capacitive materials. The moderate capacitance should come from the medium specific surface area of CNTs (120–500 m2/g), lower than that of active carbon (1000–3500 m2/g) [596]. In order to improve the power and cycle performances of CNT array electrodes, pseudo-capacitive materials (including conducting polymers, such as polyaniline [613], polypyrrole, and polythiophene, metal oxides, such as ruthenium oxide, manganese oxide [614], NiO, and Fe3O4, and nitrides, such as vanadium nitride) are deposited on the CNT surface to form CNT composite electrodes. In these CNT composite capacitors, CNTs serve as an effective support for pseudo-capacitive materials because of the excellent mechanical properties of CNTs. At the same time, the CNTs conduct electrons due to superior electrical properties. These pseudo-capacitive (or termed redox supercapacitive) materials can be fast and reversible redoxed on the CNT surfaces or near-surface for charge storage and the pseudo-capacitance is faradic. For example, the ruthenium oxidation states in ruthenium oxide can react in electrolyte as [593]

\[
\text{RuO}_2 + x\text{H}^+ + xe^- \leftrightarrow \text{RuO}_2-x(\text{OH})_x, \quad 0 \leq x \leq 2
\]  

(11)

The continuous change of \(x\) during \(\text{H}^+\) insertion leads to a pseudo-capacitive behavior with ion adsorption. The charge storage mechanism of manganese oxide is based on the surface absorption of electrolyte cations and proton incorporation:

\[
\text{MnO}_2 + x\text{C}^+ + y\text{H}^+ + (x + y)e^- \leftrightarrow \text{MnOOC}_x\text{H}_y
\]  

(12)

A study in an electrolyte ionic liquid shows that maximum capacitance is produced when the pore size is close to the ionic radius [598]. So the density of CNT array is usually very high with the gap between CNTs being a few nanometers. So, the conducting polymers and inorganic materials are usually electrodeposited on CNT arrays, like PANI [613] and MnOx [614].

Such CNT array composites have higher capacitances than CNT arrays and pseudo-capacitive materials due to the contribution of both double-layer capacitance and pseudo-capacitance (Figure 104). The capacitance of the PANI/CNTA composite is 1030 F/g at a low current density of 5.9 A/g [613], higher than the PANI materials. Compared to the best results from commercial products (about 130 F/g), the pseudo-capacitors have much higher energy storage capabilities.

The advantages of CNT arrays as capacitors come from their excellent mechanical properties, electrical conductivity, and good ion conduction owing to the straight conduction pathways [609].
5.4.3. Lithium ion batteries

In batteries, electrical energy is generated by conversion of chemical energy via a redox reaction at the anode and the cathode in a closed system. Unlike in ultracapacitors where the solvent of the electrolyte is not involved in the charge storage mechanism, the solvent of the electrolyte contributes to the solid–electrolyte interphase in batteries. The Li-ion batteries, one kind of rechargeable batteries, usually consist of an active carbon anode, a lithium–cobalt oxide cathode, and an organic electrolyte.

Activated carbon is used in the commercial lithium-ion batteries. In order to obtain better performance, CNT arrays and CNT array composites are recently studied as electrodes besides the random CNTs and random CNT composites.

Figure 105 illustrates such a Li-ion battery consisting of CNT array (composite) electrodes and a Li electrode. The CNT arrays are prepared by the PECVD method described in Section 2.1.3.
PANI/CNT array composite is used as the lithium-ion battery cathode [613]. The capacity of such PANI/CNT array composite electrode (98 mA h/g) is higher than that of the PANI/random CNT composite electrode (86 mA h/g) [615]. MnO$_x$/CNT array composite electrodes are also used as cathodes [614]. The capacity of MnO$_x$/CNT array composite (246 mA h/g) is also higher than that of MnO$_x$-based nanostructures. In the CNT array composites, the CNT array framework enhances the rate performance of the electrode materials by providing good electrical conductivity and preserving the benefits of the electrochemical properties of supercapacitive nanomaterials. The CNT array electrodes can be used as lithium-ion battery anodes [481,601]. The rate and cycle performance of CNT array electrodes are superior to random CNT electrodes.

5.4.4. **Hydrogen storage**

CNTs have been long heralded as potentially useful for hydrogen storage. It was reported that the amount of hydrogen desorbed on SWCNTs is 5–10 wt% at room temperature [616–618], close to the reasonable automotive target of 6.5 wt%. Later, a higher hydrogen storage capacity was reported and a lot of papers have been published in this field. For example, it was reported that lithium-doped SWCNTs can absorb 20 wt% of hydrogen at room temperatures under ambient pressures [619]. However, experimental reports of high storage capacities are so controversial that it is impossible to assess the true potential [318]. Careful experiments indicate that the largest absorption percentage of hydrogen is less than 0.1 wt% at room temperature in SWCNTs [620], in MWCNTs [620], and in carbon fibers [621]. Recent investigations show only a small reversible hydrogen uptake for SWCNTs [622]. More efforts are needed in the field, and the application of CNT arrays in hydrogen storage is still far away from practical applications.

5.5. **Electromechanical devices**

5.5.1. **Actuators**

Electromechanical actuators are frequently used in robots and typically comprised of two electrodes separated by an electrically insulating material, similar to the supercapacitors. The charge injection causes electrode expansions and contractions that can do mechanical work in the electromechanical actuators [623]. The maximum observed isometric actuator stress of SWCNT-sheet actuators is about 26 MPa, 100 times that of the stress generation capability of natural muscles.

5.5.2. **Artificial muscles**

Actuator materials can convert electrical, chemical, thermal, or photonic energies to mechanical energy. Electrostatic attraction and repulsion between two CNTs were used for cantilever-based nanotweezers [624] and electromechanically based logic elements [564] and nanoswitches [625]. Macroscaled CNT actuators powered by electricity [623,626,627] or fuel [628] can provide a hundred times higher stress generation than natural muscles [629]. Aligned CNT composites can also be actuators powered by IR irradiation [630] or by electricity [631], and be of shape memory functions [632,633].

Figure 106 shows the CNT aerogel sheets used as the sole component of artificial muscles. The CNT aerogel sheets are fabricated by the spinning method described in Section 2.2.3.2. Such muscles can provide giant elongations and elongation rates of 220% and $3.7 \times 10^4$% per second, respectively, at operating temperatures from 80 to 1900 K. The observed voltage dependence of actuator stroke in the width direction at length center, normalized to the initial width to provide generated strain $\Delta W/W_0$, is shown in Figure 106(c) for single and stacked aerogel ribbons having
Figure 106. Artificial muscles. (a) Photograph of a rigidly end-supported 50 mm long × 2 mm wide nanotube sheet strip. (b) Same sheet strip expanded in width by applying a 5 kV voltage with respect to ground. (c) Width-direction actuation strain, $\Delta W/W_0$ versus applied voltage for $N = 1–8$ stacks of single aerogel sheets and for a densified eight-sheet stack, labeled 1 to 8 and 8′, respectively, having $L_0 = 25$ mm and $W_0 = 2$ mm. The universal curve in the inset for this aspect ratio (12.5) shows results for un-densified nanotube sheet stacks that are normalized with a single-fit parameter $R$, where the normalization factor is $S_N = (1/N - R)/(1 - R)$. From A.E. Aliev et al., Science, 323, pp. 1575–1578, 2009 [634]. Reprinted with permission from AAAS.

### 5.6. Terahertz sources

CNTs have many properties – from their unique dimensions to an unusual current conduction mechanism – that make them ideal components of electrical circuits. For example, they have shown to exhibit strong electron–phonon resonances, which indicate that under certain direct current bias and doping conditions their current and the average electron velocity, as well as the electron concentration on the tube, oscillate at terahertz frequencies. These resonances could potentially be used to make terahertz sources or sensors.

### 5.7. Other applications

There are a handful of other applications of assembled CNTs, such as blackbody absorbers [635], vacuum microelectronic sources [361,370], and IR detectors [636,637].

### 6. Conclusions

In summary, the *in situ* and *ex situ* fabrication methods, the physics for alignment, the unique physical properties, and the broad application scale of aligned CNTs are reviewed. It has been clearly demonstrated by numerous publications that PECVD and thermal CVD are frequently the most effective methods to *in situ* grow aligned CNT arrays with a pre-determined orientation, diameter, length, location, and site density. Depending on the spatial distribution of catalytic nanoparticles on substrates, the aligned CNTs may have 1D or 3D orderings. The mechanisms for achieving alignment are discussed. Aligned CNTs have found their edges for applications in thermal, electrical, photonic, mechanical, chemical, and biological devices as well as various types
of sensors for gas and bio-specie detections. These applications are reviewed and illustrated based on the uniqueness of the aligned CNT geometry and the corresponding physical properties due to alignment.

Although there have been extensive research efforts on CNT alignment, the physics and properties, and the broad application possibilities, there still remain tremendous unfinished work and unexplored territories to realize the full potentials of aligned CNTs. It is the hope of the authors that this review can generate even broader interests from researchers of all related fields and from academic and industrial funding institutions to further explore various applications of aligned CNTs with a grand goal of improving our fundamental scientific understanding and everyday life.

Note
1. In fact, the structure of the electric double-layer is more complex than the Helmholtz model. Helmholtz model states that two layers of opposite charges are formed at the electrode–electrolyte interface and are separated by an atomic distance. Modified Gouy–Chapman model refers to a diffuse layer consisting of continuous distribution of electrolyte ions (both cations and anions), not a layer consisting of only cations or only anions, in the electrolyte solution. The modern Stern model combines the Helmoltz model with the Gouy–Chapman model to structure two regions of ion distribution: the inner compact layer (Stern layer) where ions are strongly absorbed by the electrode and an outer diffuse layer defined in the Gouy–Chapman model. The more accurate capacitance is a sum of the capacitances from the two regions: 1/C = 1/C_{Stern} + 1/C_{diff}. Both Stern layer contribution C_{stern} and diffuse layer contribution C_{diff} are proportional to the specific surface area and depend on the pore size.

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[57] Three-dimensional images are created using POV-Ray open-source software (http://www.povray.org).


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