

Advancement in Carbon Nanotubes Optoelectronic Devices for Terahertz and Infrared Applications

Yue Wang,^{*} Guangcheng Sun, Xiaoju Zhang, Xiang Zhang, and Zijian cui

Benefiting from the outstanding optical, thermal, electrical, and mechanical properties, carbon nanotubes (CNTs) hold significant potential in the fields of materials, physics, chemistry, biology, as well as emerging disciplines such as electronics and optoelectronics. This paper provides a comprehensive review of the latest developments of CNTs optoelectronic devices operating in the terahertz (THz) and infrared (IR) wave range. At the beginning of this review, the unique structural characteristics of CNTs are introduced, overviewing their fundamental electronic structure, and emphasizing their impact on optoelectronics behavior. Further, on various synthesis techniques are discussion employed for the growth of single nanotube and the preparation of CNTs films. The penultimate section, the optical properties of CNTs are analyzed within the THz and IR spectral region and overview the application of THz time-domain spectroscopy in extracting key material parameters of CNTs, and further discuss the theoretical models describing THz conductivity in CNTs. In the end, the most promising CNTs-based device concepts are highlighted for sources, detectors, modulators, absorbers, and sensors within in THz and IR frequency band. This comprehensive review provides a valuable insight into the utilization of CNTs across various aspects of THz and IR optoelectronic devices.

transition regime between typical low-energy electronics and high-energy photonics, it has the advantages of a wide frequency band, low photon energy, coherence, non-ionization, and strong penetrability to non-polar materials. However, due to the limited response of most natural materials to THz radiation, currently available microwave electronic and IR optical devices cannot be directly utilized in the THz region. This has led to a shortage of diverse THz functional devices, including compact high-power sources and sensitive detectors that can effectively operate at room temperature. Consequently, the THz band is often denoted as the “THz gap” in the electromagnetic spectrum. From a historical standpoint, THz radiation was primarily employed by astronomers, chemists, and spectroscopists throughout most of the 20th century, particularly in the domains of high-resolution spectroscopy and remote sensing. Over the past three decades, the rapid advancement of THz time-domain spectroscopy (THz-TDS) technology, coupled with the swift progress in low-scale semiconductor technology, has significantly diminished the technological gap in the THz spectrum. Optical technology has made great progress in the higher frequency range of the THz band, while microwave technology has extended into the lower bound of the THz range. THz waves are now recognized as a novel and potent tool across diverse scientific research fields, playing a crucial role in areas ranging from fundamental science to practical applications. These applications include ultra-broadband communication,^[4] holographic imaging and sensing,^[5,6] biomedicine,^[7] material characterization,^[2] condensed matter physics,^[8] astronomy,^[9] art history,^[10] and environmental monitoring.^[11]

The THz system is primarily comprised of radiation sources, detectors, and various functional devices. In these systems, THz radiation is generated and detected indirectly through the conversion of an optical beam. This process indicates that the substantial dynamic range achieved is the result of a complex and costly coherent detection approach. Despite extensive exploration of electrical, optical, and semiconductor solid-state technologies for the direct generation, manipulation, and detection of THz radiation, each approach exhibits one or more limitations that currently hinder the widespread utilization of THz science and

1. Introduction

Terahertz (THz) waves are typically characterized as electromagnetic waves within the frequency range of 0.1 to 30 THz ($1 \text{ THz} = 10^{12} \text{ Hz}$). Occasionally, a more inclusive definition is employed, encompassing electromagnetic waves up to 100 THz. This broader definition spans the entirety of the middle and far-infrared (IR) band.^[1–3] Since THz waves occupy a special

Y. Wang, G. Sun, X. Zhang, X. Zhang, Z. cui
Key Laboratory of Ultrafast Photoelectric and Terahertz Science in Shaanxi Xi'an University of Technology
Xi'an 710054, China
E-mail: wangyue2017@xaut.edu.cn

X. Zhang
Engineering University of Technology of PAP
Xi'an, Shaanxi 710086, China

The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/aelm.202400124>

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technology. As the cornerstone of THz science and technology, research on THz functional devices is ongoing and has entered a new stage of development. Consequently, there is an urgent requirement for novel and highly efficient THz devices based on new concepts, architectures, and materials to facilitate the further advancement and broad application of THz technology.

Recently, significant progress in advanced materials and nanofabrication technology have opened new possibilities for the development of THz devices. The active materials employed in THz devices have transitioned from traditional semiconductor materials^[12,13] to superconducting materials,^[14] liquid crystals,^[15] and more recently, to new low-dimensional materials.^[16–20] Carbon nanotubes (CNTs), as nearly ideal 1D nanomaterials, have emerged as a next-generation high-performance nanoelectronic, photonic, and optoelectronic material applied in the field of scanning probe microscopes,^[21] transparent conductive films,^[22] energy harvesting and storage,^[23,24] and drug delivery and optical probes in biomedicine.^[25,26] The remarkable properties of CNTs enable them to perform multiple functions within a single material, including signal emission, transmission, modulation, and detection. The unique combination of nanoscale lateral dimensions and high aspect ratios, ranging from 10^2 to 10^7 for CNTs, results in exceptional optical and electrical properties. These properties include high charge-carrier mobility ($>10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}$ at room temperature),^[27] strongly anisotropic optical absorption,^[28] and ballistic transport.^[29] This positions CNTs as ideal nanoscale building blocks for a new generation of high-performance devices operating across the far-infrared band. Most importantly, CNTs exhibit a plasma frequency that aligns with the THz frequency band.^[30–32] This property positions CNTs as promising candidates for developing metamaterial THz devices with active tunability.

In the first section of this review, we discuss the fundamental properties of single-walled CNTs (SWCNTs), including their tubular structure, electronic structure, preparation, and post-treatment process. These factors collectively determine their electronic properties, as well as their optical behavior when subjected to an external THz electric field. Section 2 describes optical selection rules of SWCNTs, principles of material parameter extraction using the THz-TDS system, and methods of conductivity and photoconductivity fitting by the various physical model. In the third part, we focus on THz devices enabled by CNTs, including emitters, modulators, detectors, absorbers, and metamaterial devices, and highlight both pioneering early work and more recent discoveries in this area. The review concludes in section 4 with a summary of the key points discussed and provides a perspective on the challenges, research directions, and prospects within the field of THz devices enabled by CNTs.

2. Structure and Basic Properties of CNTs

2.1. Structure of CNTs

CNTs, as the name implies, are unique tubular structures of nanometer diameter made entirely of carbon, with an aspect ratio (defined as the ratio of length to diameter) of exceeds 10 000, thus

can be considered as a prototypical system of 1D structure.^[33–36] The nanotubes can capable of forming concentrically arranged graphite shell structures bonded by strong van der Waals force, with the adjacent shells slightly larger than the interlayer distance of graphite.^[37,38] Single shell nanotubes are known as SWCNTs, and nanotubes with more than one shell are referred to multi-walled carbon nanotubes (MWCNTs) accordingly, as shown in **Figure 1a,b**. CNTs hold unprecedentedly small diameters ranging from a few nanometers to several hundred nanometers. At present, individual CNTs with a length extending over half a meter has been successfully synthesized.^[39] The two ends of CNTs are usually enclosed by dome-shaped semi-fullerene caps (pentagonal ring defect), each containing six five-membered rings (**Figure 1a**). In addition, SWCNTs are apt to self-organize into nanotube bundles containing tens to hundreds of nanotubes nearly uniform in diameter (**Figure 1c**). In a bundle of structures, SWCNTs are arranged periodically in a hexagonal lattice to form a crystal-like construction.^[40]

Topologically, SWCNTs can be envisioned as a two-dimensional (2D) graphene sheet rolled up to form a hollow and seamless tubular structure.^[36] Graphene is a 2D hexagonal lattice of carbon atoms as depicted in **Figure 2a,b** with the nearest-neighbor distance between carbon-carbon atoms by $a = 1.42 \text{ \AA}$. The unit cell of graphene is spanned by the two basic vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ and contains two carbon atoms marked A and B, where the length of primitive lattice vector $|\mathbf{a}_1| = |\mathbf{a}_2| = 2.461 \text{ \AA}$ form an angle of 60° . Graphene lattice vector $\mathbf{C}_h = n\mathbf{a}_1 + m\mathbf{a}_2 \equiv (n, m)$, where n and m represent integers and $0 \leq |m| \leq n$, denotes the relative position between any two carbon atoms on the graphene honeycomb lattice.^[37,41] A SWCNTs can be created by wrapping a graphene sheet so that the two crystallographically equivalent carbon atoms connected by vector $\mathbf{C}_h$ encounter. $\mathbf{C}_h$ will become the circumference of SWCNTs, thus also called circumferential vector or chiral vector.

When the chiral vector $\mathbf{C}_h$ is completely coincident with primitive lattice vectors $\mathbf{a}_1$, CNTs of the species $(n, 0)$ are classified as zigzag type, as depicted in **Figure 1e**. If the circumferential vector $\mathbf{C}_h$ is located exactly along the direction between the two primitive lattice vectors, corresponding to the type (n, n) , such CNTs are referred to as armchair type, as illustrated in **Figure 1f**. The rest of the CNTs with $(n, m \neq n \neq 0)$ are called as chiral or helical nanotubes, as shown in **Figure 1d**. Both armchair and zigzag nanotubes host a mirror plane and thus are considered achiral, in contrast with general chiral tubes that have no mirror plane.

2.2. Electronic Structure of SWCNTs

The electronic dispersion relation and electronic density of states (DOS) of SWCNTs can be explained in a good approximation by zone-folding that of graphene.^[34,35,42,43] In analogy with graphene, SWCNTs are characterized by two types of bonds, which exhibit so-called planar sp^2 hybridization. Every carbon atom has four valence electrons occupying the $2s$, $2p_x$, $2p_y$, and $2p_z$ atomic orbitals. The hybridization of $2s$, $2p_x$, and $2p_y$ electrons form in-plane σ bonding and σ^* antibonding, while the remaining $2p_z$ electron creates delocalized π bonding and π^*

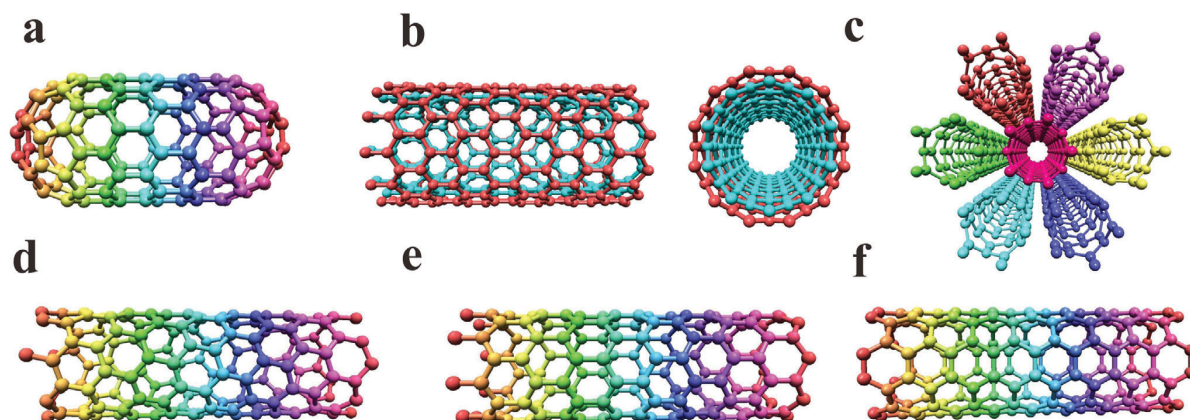


Figure 1. Schematic diagram of the spatial structure of CNTs. a) A SWCNTs whose two ends are sealed with semi-fullerene caps. b) Front view (left) and side view (right) of MWCNTs. c) A nanotube bundle consisting of six SWCNTs. d) A (7, 2) chiral SWCNTs. e) A (8, 0) zigzag SWCNTs. f) A (5, 5) armchair SWCNTs.

antibonding. In the tight-binding model, considering only the nearest-neighbor C-C atom interaction, the electronic band structure of graphene is given by:^[44]

$$\varepsilon_{\pm}(k) = \pm\gamma_0 \sqrt{1 + 4 \cos \frac{\sqrt{3}k_x a}{2} 4 \cos \frac{k_y a}{2} + 4 \cos^2 \frac{k_y a}{2}} \quad (1)$$

where γ_0 denotes the interaction energy between the nearest neighbor C-C atoms, and $\pm$ sign corresponding to the upper (π) and lower (π^*) band in the reciprocal space. The resulting electronic dispersion relation of graphene (Figure 2c,d) is characterized by the valence band and the conduction band touching each other at six points at the corner of the hexagonal first Brillouin zone (BZ).

The tangential component of the electron wave vector around the circumference of SWCNTs is quantized owing to the confinement of periodic boundary conditions, giving rise to the formation of a series of discrete energy subbands. In contrast, electron motion along the nanotube axis is remain free, thus the longitudinal component of the electron wave vector is a continuous variable. Mapping these discrete allowed vectors for (n, m) SWCNTs to the extended 2D BZ of graphite sheet yields a set of parallel lines whose length, number, and direction are determined by the circumferential vector $C_h(n, m)$ of SWCNTs. The 1D electronic band structure of SWCNTs can be written as follow:^[35,37,45]

$$E_{\mu}(k) = E_{g2D} \left(k \frac{K_2}{|K_2|} + pK_1 \right) \quad (2)$$

$$(p = 0, \dots, N-1, \text{ and } -\pi/T < k \leftarrow \pi/T) \quad (3)$$

where vectors K_1 and K_2 can be calculated via the reciprocal-lattice basic vectors $b_1 = \frac{2\pi}{a}(\frac{1}{\sqrt{3}}, 1)$ and $b_2 = \frac{2\pi}{a}(\frac{1}{\sqrt{3}}, -1)$ as follow:

$$K_1 = \frac{1}{N}(-t_2 b_1 + t_1 b_2) \quad (4)$$

$$K_2 = \frac{1}{N}(mb_1 - nb_2) \quad (5)$$

Here, $t_1 = (2m+n)/d_R$, $t_2 = -(2n+m)/d_R$, d_R represent the greatest common divisor of $2m+n$ and $2n+m$. If the chiral index of the nanotube satisfies the condition: $\text{mod}(2n+m, 3) = 0$, then cutting lines touching the K or K' point in the BZ of graphene and such nanotube will be metallic. Furthermore, these metallic SWCNTs (m-SWCNTs) can be reclassified as metal-1, metal-2p and metal-2m depend on whether $\text{mod}(3m/d_R, 3) = 0, 1$ or 2. In the case of metal-1 SWCNTs, the Fermi level is located at the Γ point of 1D BZ, whereas for metal-2 SWCNTs, the Fermi energy is located at 1/6 (or 5/6) position on a cutting line for metal-2p (or metal-2m) are depicted in Figure 2e.^[45] The cutting lines of the nanotube conforming to $\text{mod}(2n+m, 3) = 1$ or 2 bypass the K or K' point and will be semiconducting. Type-I ($\text{mod}(2n+m, 3) = 1$) semiconducting SWCNTs (s-SWCNTs) exhibit an analogous photoluminescence energy spectrum, which is completely different from that observed in type-II ($\text{mod}(2n+m, 3) = 2$) s-SWCNTs. A map of the chiral index and the classification of m- and s-SWCNTs are shown in Figure 2f, where one-third of SWCNTs are m-CNTs while the rest are s-CNTs taking into account all the chiral SWCNTs. In particular, (n, n) armchair tubes belong to metal-2p SWNTs, while $(n, 0)$ zigzag nanotubes are metal-1 only in the case where n is a multiple of 3.^[45] Figure 3a,c show the calculated band structures of two typical chiral nanotubes. The conduction and valence bands of (8, 2) nanotube intersect at the Fermi level of 0 eV, showing metallic properties. By contrast, (4, 2) nanotube is semiconducting nanotube with certain energy gap.

The DOS is of particular significance in understanding and verifying the electronic band structure of SWCNTs, which is defined as the number of allowed states per unit of energy for a given energy interval ΔE ($\Delta E \rightarrow 0$).^[46] The DOS is known to be highly dependent on the dimension of the system, diverging as the inverse of a square root in 1D systems. The 1D quantum-confined electronic state in the SWCNTs is expected to exhibit diverging DOS close to band extrema. The DOS of per carbon

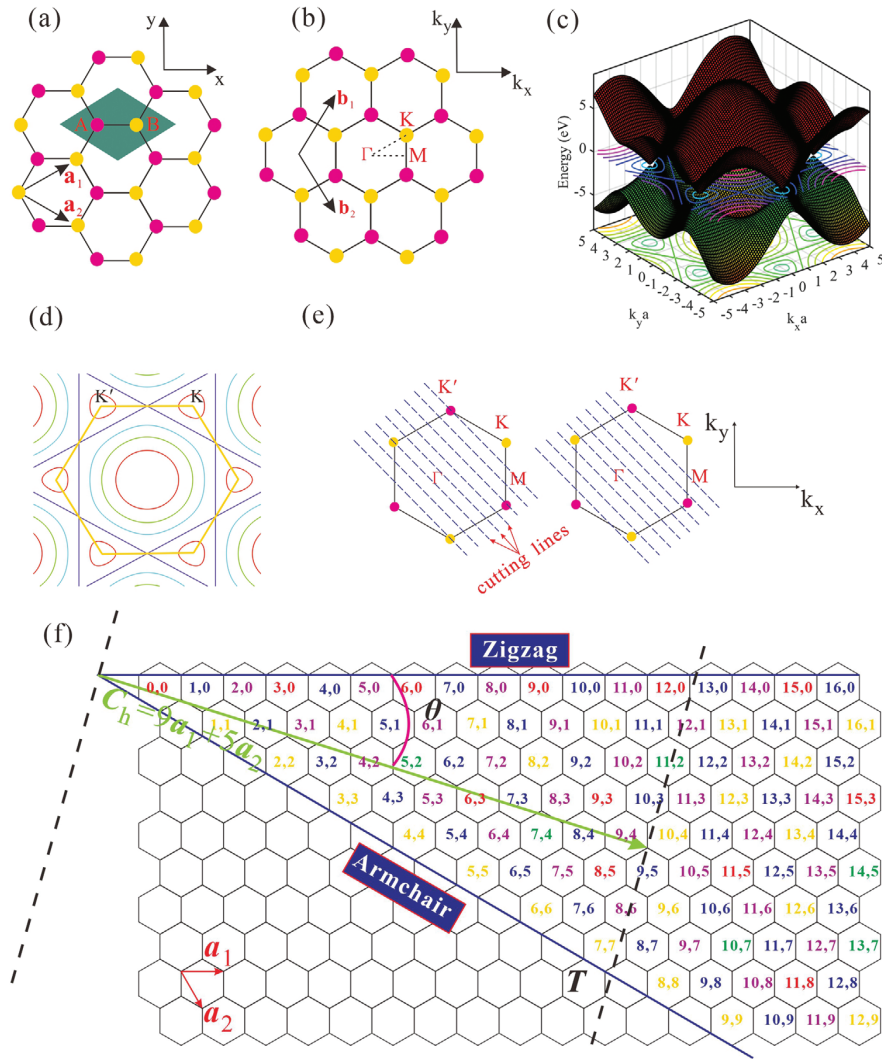


Figure 2. The schematic diagram of CNTs mapped from graphene sheets. Schematic diagram of lattice a) and reciprocal space b) of graphene. c) Diagram of the band structure of graphene, and the corresponding 2D projection map. e) Schematic diagram of forming metallic and semiconducting CNTs. f) The formation and classification of (n, m) SWCNTs. Purple and blue (n, m) denote type I and type II semiconducting nanotubes, respectively. Red, yellow, and green (n, m) represent metal-1, metal-2p, and metal-2m nanotubes, respectively. The appearance of the metallic SWCNTs is not periodic except for zigzag and armchair SWCNTs.

atom in the vicinity of the Fermi level of all chiral SWCNTs was formulated by Mintmire and White as:^[47]

$$D(E) = \frac{2\sqrt{3}a}{\pi^2 d \gamma} \sum_{m=1}^N \frac{|E|}{\sqrt{E^2 - \epsilon_m^2}} \quad (6)$$

where $\epsilon_m = |3m+1|\frac{a\gamma}{d}$ for s-SWCNTs and $\epsilon_m = |3m|\frac{a\gamma}{d}$ for m-SWCNTs, d represents the diameter of the nanotube, and $d = \frac{|C_h|}{\pi} = \frac{a}{\pi} \sqrt{n^2 + nm + m^2}$. The expression for DOS of SWCNTs indicates sharp 1D van Hove singularities at the energy band edges when $E = \epsilon_m$ and $\epsilon_m \neq 0$ consistent with the expected result of DOS in a 1D system. Moreover, in the case of

m-SWCNTs, the $m = 0$ band give rise to a nonzero DOS between the first van Hove singularities where the Fermi level lies (Figure 3b), with $D(E_F) = \frac{2\sqrt{3}a}{\pi^2 d \gamma}$. By contrast, s-SWCNTs have no DOS at the Fermi energy level (Figure 3d). Note that the separation between the first van Hove spikes in the DOS of m-SWCNTs is three times greater than that of s-SWCNTs.

2.3. Preparation of CNTs Films

Since MWCNTs were firstly discovered by Iijima in the cathode product of C_{60} grown by the arc discharge method,^[48] extensive research has been conducted to develop preparation

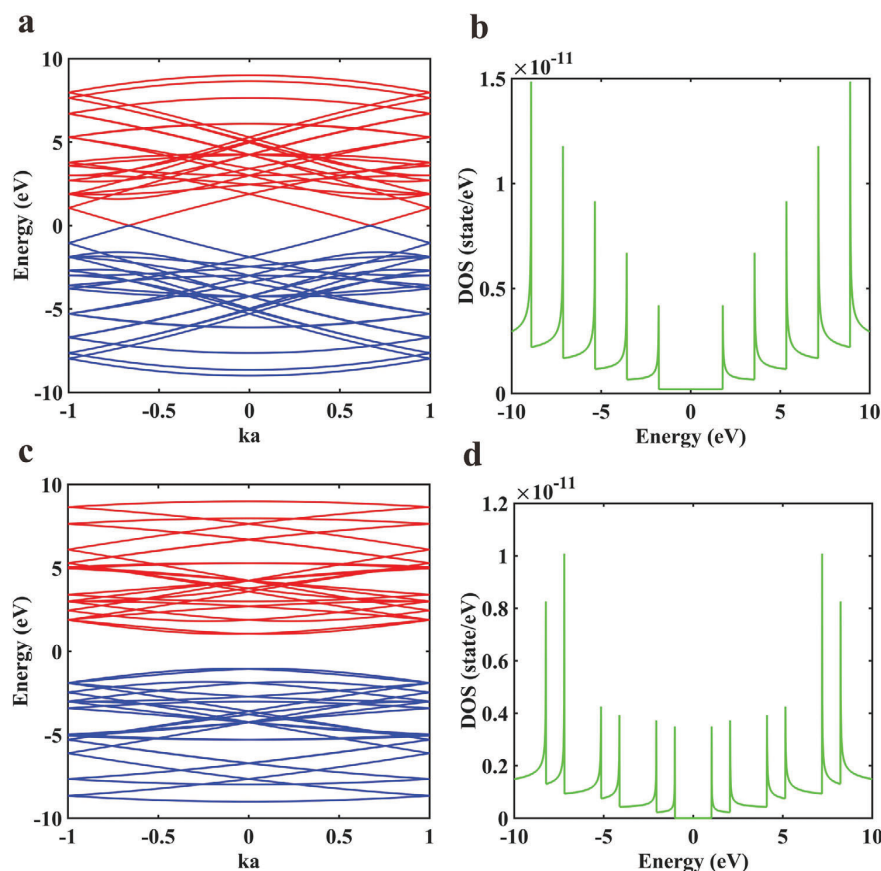


Figure 3. The bandgap structure a, c) and DOS b, d) of (8, 2) metallic and (4, 2) semiconducting SWCNTs.

methods that offer high yield, uniform tube diameter, few structural defects, low impurity content, relatively low cost, and convenient operation. Several techniques have been explored for fabricating CNTs such as electric arc discharge,^[49] laser ablation,^[50] chemical vapor deposition (CVD),^[51] plasma torch method/thermal plasma method,^[52] ball milling/high energy milling/mechanical alloying,^[53] liquid electrolysis method,^[54] hydrothermal synthesis/sonochemical,^[55] spray pyrolysis,^[56] catalytic decomposition of hydrocarbons,^[57] low-temperature solid pyrolysis,^[58] and green methods.^[59] This section covers the various mainstream approaches to fabricate CNTs including electric arc discharge, laser ablation, and CVD.

As a kind of 2D carbon nanomaterials, CNTs films^[60] have the advantages of excellent electrical^[61] and thermal conductivity,^[62] outstanding mechanical and chemical stability,^[63] good flexibility and structure, and easy to control and preparation in a large area. As a result, CNTs films have emerged in THz and IR region and have been rapidly developed, which may bring revolutionary changes to the application and development of the related functional devices. Presently, the fabrication approaches of CNTs films contain dry/wet methods, each offering unique advantages.

2.3.1. Dry Methods

For the dry methods, the whole process of the CNTs films preparation is not in contact with liquid. Generally, two dry methods which are on the basis of floating catalyst CVD (FCCVD)^[64] and drawing CNTs yarns from aligned CNTs array are used to process CNTs films.^[65] FCCVD can be applied for synthesizing CNTs with various structures including single-wall, double-wall, and multi-wall CNTs.

CNTs synthesized through FCCVD can undergo self-assembly to form films, fibers, and bulk structures by adjusting experimental conditions and collection methods.^[66] Li et al. developed a winding apparatus connected to a FCCVD reactor for film collection and compositing. This innovative approach allowed for the fabrication of free-standing CNT films with controlled thickness.^[67] Zhang et al. synthesized high-quality SWCNT thin films by FCCVD, and transferred the films on polyethylene terephthalate (PET) by dry or direct process as transparent heaters in 2022.^[68] However, significant challenges persist, including issues related to the controlled-growth mechanism,^[69] uniformity of CNTs,^[70] mass production,^[71] and large-area CNTs films preparation.^[72] In addition, Jiang et al. demonstrated that CNTs can be self-assembled into yarns simply by drawing out

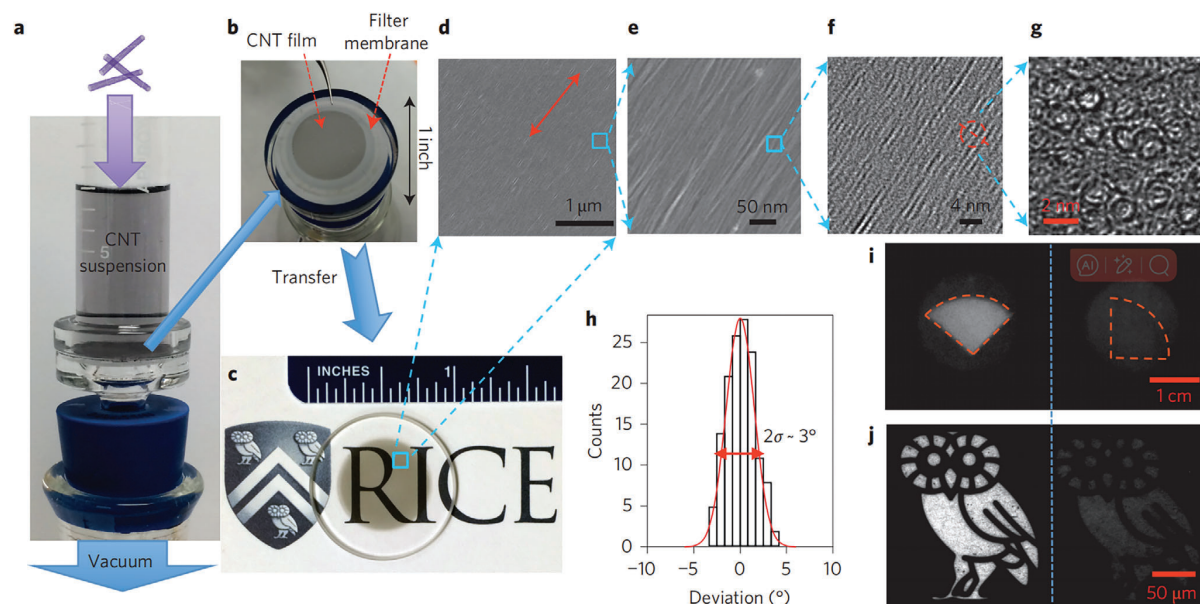


Figure 4. Preparation and characterization of Macroscopically aligned wafer-scale crystalline SWCNTs films. a) The uniformly dispersed SWCNTs suspension passes through the vacuum filtration system at a very slow speed. b) An aligned wafer-scale SWCNTs film is deposited on a filter membrane in a straightforward manner. c) Optical picture of the fabricated SWCNTs film transferred to a transparent substrate. d) A scanning electron microscopy (SEM) image, e) a high-resolution SEM image, f) a top-view transmission electron microscopy (TEM) image, and g) a high-resolution cross-sectional TEM image of the produced SWCNTs film. h) Angular distribution of SWCNTs in a cross-sectional area of 1 μm², indicating the prepared films are globally aligned within ±1.5°. The produced SWCNTs film show strong optical anisotropy both on a macroscopic scale i) and a microscopic scale j). Reproduced with permission.^[85] Copyright 2016, Springer Nature.

from the super-aligned arrays of CNTs.^[65] The CNTs films prepared by the spinning process have excellent electrical conductivity and good flexibility, and can freely control the formation of cross-stacked structures,^[73] which is conducive to a wide range of applications in flexible electronics.

2.3.2. Wet Methods

In general, the wet method involves collecting the dispersed CNTs from an aqueous or organic suspension, and then drying the suspension.^[74] This wet process shows advantages such as a low-temperature process and the absence of a requirement for vacuum conditions. Moreover, the wet process expands the range of substrate options, encompassing materials like plastic, polyimide and polyethylene terephthalate. In addition, a well-prepared CNTs suspension is the key condition for all wet methods which directly affects the quality of the film. The key process of wet methods usually contains three steps. The first step is to prepare the suspension. The second step, deposit the CNTs film. The third step is the post-treatments process involves removing surfactants or doping.^[75] The wet methods of preparation of CNTs films can be divided into Langmuir-Blodgett (LB),^[76] Langmuir-Schaefer (LS),^[77] self-assembly method (SA),^[78] electrophoretic deposition (EPD),^[79] spraying,^[80] vacuum filtration,^[81] printing^[82] and bubble blowing.^[83]

Heer et al. introduced the concept of filtration-induced alignment of CNTs. They produced a CNTs film by drawing a dispersed CNTs suspension through a ceramic filter with a pore size of 0.2 μm. After being transferred to a plastic surface, the surface is rubbed with alumina foil or thin Teflon sheet to align the CNTs along the rubbing direction.^[84] Wu et al. proposed vacuum filtration method for fabricating pure transparent SWCNTs film and transferred to various substrates in 2004.^[74] In 2016, He et al. developed a modified filtration technique for the preparation of aligned SWCNTs.^[85] According to literature reports, the wafer-scale aligned SWCNTs films can be fabricated by slow vacuum filtration (Figure 4). The thickness of the film could be controlled to a few nanometers to 100 nm. The authors employed the slow vacuum filtration process to prepare ideal polarizers in the THz band. In addition, highly aligned and chirality-enriched CNTs film devices were fabricated by combining the approach with the sorting techniques.

One notable application of CNTs is as a semiconducting ink to print massive and flexible electronic devices.^[86] Printing technology has become an attractive option for many large-area applications due to its advantages in eliminating numerous high-cost, low-throughput processing steps. Moreover, printed processes are highly compatible with non-traditional flexible substrates such as paper and polymers. One popular printing method is inkjet printing, which can print various functional inks, including semiconductors, conductive and insulating materials.^[87] With the continuous development of inkjet printing technology, 3D printing has emerged. This method enables the full

printing of 3D structures through a layer-by-layer inkjet-printing process.^[88]

2.4. Purification and Separation of CNTs

The polydispersity issue of CNTs is critical due to the high dependence of their electronic structure on the diameter and chiral vector. Despite the development of synthetic approaches aimed at selectively growing SWCNTs in high production, the as-grown SWCNTs consist of a mixture of metallic and semiconducting SWCNTs with a wide diameter and chirality distribution. Even developed methods that can achieve a narrow range of diameter still face challenges in sorting the electronic types, as many metal and semiconductor chiral CNTs exhibit nearly identical diameters.^[89]

The semiconducting purity of SWCNTs is a crucial factor influencing their application in electronics. Therefore, the separation of metallic and semiconducting SWCNTs is fundamental for achieving structural separation. Various attempts, including controlling breakdown,^[90] electrophoresis,^[91] polymer wrapping,^[92] aqueous two-phase extraction,^[93] selective chemical reactions,^[94] and chromatography,^[95] have been carried out to remove the metallic and/or semiconducting SWCNTs from the mixed SWCNTs.

In 2022, Liu et al. reported the use of a cholate derivative, sodium hydoxycholate (SHC), for the separation of metallic and semiconducting SWCNTs.^[92] At present, density gradient ultracentrifugation (DGU) achieves separation of diameter and electronic type by adjusting the concentration of the surfactant.^[96] Moreover, DGU can be applied for sorting of individual SWCNTs chiralities,^[97] double-walled CNTs,^[98] and SWCNTs enantiomers by utilizing ionic and non-ionic surfactants.^[99] Owing to the advantages of simplicity, low cost, and high scalability, the aqueous two-phase technique (ATP) has attracted great attention and has been employed for separating the structure of SWCNTs. In this technique, more hydrophobic polyethylene glycol (PEG) and less hydrophobic dextran (DX) were used as the top and bottom phases, respectively.^[100]

The separation of single-chirality SWCNTs presents greater challenges compared to that of metallic and semiconducting SWCNTs, as it requires higher-resolution separation techniques. Drawing inspiration from the methods used for metallic and semiconducting SWCNTs separation, various techniques have been applied for separating single-chirality SWCNTs. These techniques include polymer wrapping, DGU, ATP, and gel chromatography.^[101–105] The chirality resolution of each separation technique varies, resulting in differences in the purity and quantity of single-chirality SWCNTs obtained through different processes.

2.5. Patterning of CNTs Films

The exceptional characteristics of CNTs films make them suitable for various electronic and optoelectronic devices. However, a major challenge in translating the excellent characteristics of CNTs films into macroscale devices is the scalable placement of CNTs into desired micro/nanopatterns and structures. Therefore, researchers aim to discover CNTs patterning techniques that

can be applied in devices for the excellent performance while being used for large-scale production. Various techniques are available for patterning CNTs films, including patterning from CNTs dispersions,^[106] subtractive CNTs patterning,^[107] pre-synthesis patterning,^[108] and patterning during synthesis.^[109]

Various dispersion-based techniques can be employed for patterning CNTs film, such as inkjet printing,^[110] gravure printing,^[111] screen printing,^[112] electrohydrodynamic jet printing,^[113] aerosol jet printing,^[114] and flexographic printing. These methods can easily pattern the conductive CNTs films on the flexible substrates, making them suitable for the fabrication of flexible devices. However, the concentration limitations of CNTs inks will result in a decrease in the density of deposited CNTs at faster throughputs, impacting device performance. To address this problem, other methods such as substrate modification patterning,^[115] template patterning,^[116] dielectrophoresis (DEP) patterning,^[117] SA,^[118] DNA-assisted assembly,^[119] dip pen nanolithography (DPN),^[120] and other novel methods have been reported to use for patterning of CNTs films.^[106,121]

Subtractive CNTs patterning refers to manufacturing processes that involve removing CNTs from a thin film to create different desired pattern. Unlike other patterning techniques which require control over density and alignment, subtractive patterning offers a significant advantage in this regard. Various subtractive methods include: poly(dimethylsiloxane) (PDMS)-based pattern modification,^[107] lithography,^[122] plasma etching,^[123] and laser ablation.^[124]

CNTs produced through CVD method can be assembling desired patterns at the location of the growth catalysts, which incorporates the patterning step before the growth of the CNTs.^[108,125] This pre-synthesis patterning technique offers the advantage of fabricating high-density CNTs patterns without facing aggregation issues encountered in CNTs dispersions. However, one significant weakness of these techniques is the high-temperature environment required for the synthesis process, limiting the selection of substrates. This constraint hinders the application of pre-synthesis patterning techniques in the back-end-of-line processes.

Different from the pre-synthesis patterning, various methods can be used to control the growth direction of the CNTs, which is important for the applications of CNTs to connect specific regions in devices or arrange in specific directions. For example, Terrones et al. observed that the CNTs grew well aligned when they grew from pattern lines of cobalt (Co) catalyst nanoparticle on a silica substrate.^[126] Controlled electric fields play a decisive role in the growth direction of CNTs during thermal CVD.^[127] This technique was successfully demonstrated by growing well aligned SWCNTs with an electric field.^[109]

3. Optical Properties of CNTs in THz and IR Frequency Range

3.1. Material Parameter Extracted by THz Time-Domain Spectroscopy

THz-TDS technology was first proposed by Auston et al in the 1980s and is called coherent far-infrared spectrometric measurement.^[128] A typical THz-TDS system utilizes short pulses of broadband THz radiation excited by femtosecond

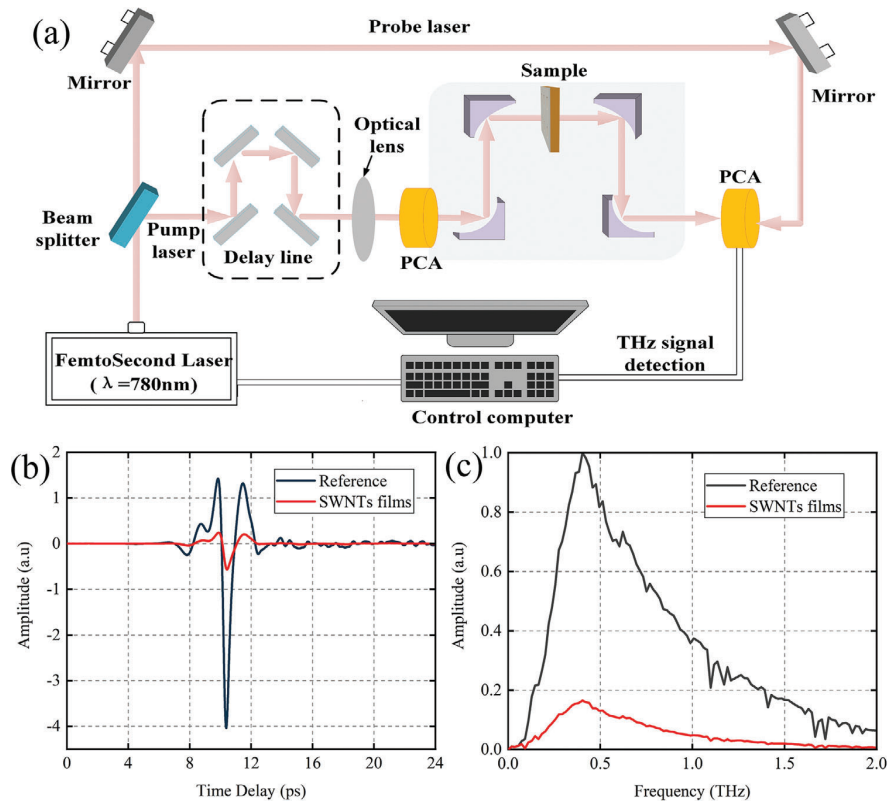


Figure 5. Principle and results of optical constants extraction of CNTs films by THz-TDS system. a) Schematic diagram of the THz-TDS experimental setup. b) THz time-domain signals of SWCNTs thin films (red curve) and reference (blue curve). c) The frequency-domain spectra. Reproduced with permission.^[132] Copyright 2022, Royal Society of Chemistry.

lasers, usually a mode-locked Ti: sapphire lasers with delivers pulses of less than 100 fs duration at 800 nm central wavelength or Er-doped fiber lasers at a wavelength near 1550 nm.^[129–131] In **Figure 5a**, the light beam is separated by a beams-splitter into two paths: the pump beam and the detection beam.^[132] In the THz optical path, four off-axis parabolic mirrors are used to form two groups of $4f$ systems, the f represents the focal length of the parabolic mirrors. The first set of $4f$ systems collimates the THz wave and refocuses it on the sample to be tested, while the remaining pair of parabolic mirrors recollect and focus the THz radiation through the sample on the THz detector. In order to solve the absorption and attenuation of electromagnetic radiation in the THz frequency band by the atmosphere, the THz optical path is usually sealed with dry gas or nitrogen gas. By changing the time delay between the THz source and detector, the time-domain waveform of THz pulses can be collected. Subsequently, a fast Fourier transform is performed to obtain amplitude and phase information of the sample and reference THz frequency domain spectra, respectively.

THz waves are capable of penetrating low absorption materials such as highly transparent CNTs films with very little attenuation. In addition, the method of extracting material optical parameters from the transmission THz spectrum is more mature than that of the reflection THz spectrum.^[133] Therefore, the transmission

THz-TDS system is more applicable to characterize the complex dielectric constant, index of refraction, and conductivity of CNTs films in the THz region. A transmission function of the sample, $T(\omega)$, is obtained by deconvolving the received spectrum with respect to the reference spectrum (Figure 5b).^[134,135]

$$T(\omega) = \frac{E_{\text{sam}}(\omega)}{E_{\text{ref}}(\omega)} = \frac{4\tilde{n}_{\text{sam}}\tilde{n}_{\text{air}}}{(\tilde{n}_{\text{sam}} + \tilde{n}_{\text{air}})^2} \cdot \exp\left[-i(n_{\text{sam}} - n_{\text{air}})\frac{\omega d}{c}\right] \cdot \exp\left[-\kappa_{\text{sam}}\frac{\omega d}{c}\right] \quad (7)$$

where $E_{\text{sam}}(\omega)$ and $E_{\text{ref}}(\omega)$ are the complex frequency spectra of the sample and the reference, respectively. The complex refractive index $\tilde{n}_{\text{sam}} = n_{\text{sam}} + i\kappa_{\text{sam}}$ is composed of two components: n_{sam} is a real part of the refractive index and κ_{sam} is an absorption coefficient. For the case of perpendicular incidence, the $\tilde{n}_{\text{air}}$ is set to 1. ω is the angular frequency of the incident light, d is the propagation distance of electromagnetic waves in the medium, c denotes the velocity of light. Hence:

$$n_{\text{sam}}(\omega) = -\frac{c}{\omega d} \left\{ \arg[T(\omega)] - \arg\left[\frac{4\tilde{n}_{\text{sam}}\tilde{n}_{\text{air}}}{(\tilde{n}_{\text{sam}} + \tilde{n}_{\text{air}})^2}\right] \right\} + 1 \quad (8)$$

And

$$\kappa_{\text{sam}}(\omega) = -\frac{c}{\omega d} \left\{ \ln[T(\omega)] - \ln \left[\frac{4\tilde{n}_{\text{sam}}\tilde{n}_{\text{air}}}{(\tilde{n}_{\text{sam}} + \tilde{n}_{\text{air}})^2} \right] \right\} \quad (9)$$

Equations (8) and (9) are in the form of a fixed-point iteration in 2D. By selecting the appropriate initial value of $n_{\text{sam}}(\omega)$ and $\kappa_{\text{sam}}(\omega)$ for the complex refractive index, the function $n_{\text{sam}}(\omega)$ and $\kappa_{\text{sam}}(\omega)$ maps those points to new points. The new values of $n_{\text{sam}}(\omega)$ and $\kappa_{\text{sam}}(\omega)$ are repeatedly substituted into the two equations to obtain the updated values until the function converges. Furthermore, the frequency-dependent dielectric function of the sample is related to the complex refractive index with the following form (Figure 5c):

$$\tilde{\epsilon}_{\text{sam}}(\omega) = (n_{\text{sam}} + i\kappa_{\text{sam}})^2 \quad (10)$$

The complex conductivity can be retrieved from $\tilde{\epsilon}_{\text{sam}}(\omega) = \epsilon_{\infty} + i\tilde{\sigma}_{\text{sam}}(\omega)/\omega\epsilon_0$, therein real and imaginary parts are $\text{Re}[\sigma_{\text{sam}}(\omega)] = 2\omega n\kappa_{\text{sam}}\epsilon_0$ and $\text{Im}[\sigma_{\text{sam}}(\omega)] = [\epsilon_{\infty} - (n^2 - \kappa^2)]$, respectively. Here, ϵ_{∞} represent the dielectric constant of the sample at infinitely large frequencies, and ϵ_0 is the permittivity of vacuum.

3.2. Physical Models of THz Conductivity in CNTs

3.2.1. Drude Model

The Drude model, referred to as the Drude–Lorentz (D–L) model or Drude-classical oscillator model, is the simplest approach to describe the frequency-dependent conductivity of metals and semiconductors. Although its simplicity, it has been proven to describe the response of free carriers to external electromagnetic waves well in the broad frequency range from MHz to the visible.^[136] Such a model assumes that the forced oscillation occurs in the free-electron system under the electric field of incident light. The free electrons undergo collisions or scattering events that randomize their momentum with damping coefficient γ_D . γ_D denotes the mutual frequency of collision used in the D–S model, and the inverse of γ_D is the average lifetime τ_D of the electrons. D–L model assumes that the displacement x of free carriers with respect to equilibrium position under the external electric field can be written as the following partial differential equation.

$$\frac{d^2x}{dt^2} + \gamma_D \frac{dx}{dt} = \frac{eE_0 \exp(-i\omega t)}{m^*} \quad (11)$$

Here e is the elementary charge, E_0 is the amplitude of the incident electric field, and m^* is the charge carrier. The dielectric response function ϵ_D can be obtained from the definition of the polarization $P = Ne\chi = \epsilon_0\chi E$, N is charge carrier density, $\chi = \epsilon_D - 1$ is polarizability. This yields the well-known Drude response:

$$\epsilon_D(\omega) = \epsilon_{\infty} - \frac{\omega_p^2}{\omega^2 + i\gamma_D\omega} \quad (12)$$

where $\omega_p^2 = Ne^2/m^*\epsilon_0$ represents a characteristic frequency of the system, also known as the plasma frequency. We can also write the Drude response in terms of the complex conductivity:

$$\sigma_D(\omega) = \sigma_{\text{dc}} \frac{i}{\omega + i\gamma_D} \quad (13)$$

in which parameter $\sigma_{\text{dc}} = Ne^2/\gamma_D m^*$ is defined as dc conductivity within the D–L model.

3.2.2. Lorentzian Oscillator

The Lorentzian oscillator, also known as D–L model with a restoring force, can be considered as a straightforward generalization of the D–L model described above in which the free carriers are simultaneously subject to a restoring force and an external electromagnetic wave. The Drude model cannot explain several transport phenomena such as backscattering of electrons, surface depletion and accumulation fields, carrier localization, and polarization in nanotubes due to the finite nanoscale dimensions of nanotubes.^[137] An extension to the D–L model can accurately reproduce the conductivity response of the semiconductor at a finite frequency. The restoring force can be offered electrostatically, for example by a surface depletion or accumulation field, as is frequently occurring near the interfaces of semiconductors. The Lorentzian oscillator is therefore appropriate to model the complex conductivity in semiconducting nanotubes. In this model the conductivity spectra can be described as follows:

$$\sigma_L(\omega) = \frac{Ne^2}{m^*} \frac{i\omega}{\omega^2 - \omega_0^2 + i\omega\gamma_L} \quad (14)$$

where ω_0 is the intrinsic resonant angular frequency of the simple harmonic oscillator, γ_L determines the width of the resonance in Lorentzian model. According to particular geometrical dependence, resonant frequency ω_0 can be linked to the plasma frequency ω_p .

$$\omega_0 = \sqrt{g}\omega_p = \sqrt{g} \frac{Ne^2}{m^*\epsilon_0} \quad (15)$$

where g is a geometrical factor. Under the assumption that all electrons are located on the surface of nanotubes $g = 0$ for the electric field E of incident light along the nanotube axis and the electronic wavevector q around the circumferential direction, $g = 1/2$ if both E and q around the circumferential direction, and $g = 1/3$ when E around circumferential direction and q along tubes axis.^[138]

3.2.3. Drude–Smith Model

The Drude Smith (D–S) model is commonly used to model the conductivity of charge carriers in restricted motion.^[12] Unlike the D–L response, which is only applicable to isotropic carrier scattering, the D–S response can describe carrier scattering in preferential directions. The collisions are assumed to be randomly distributed in time within the D–S model, and the parameter c_n

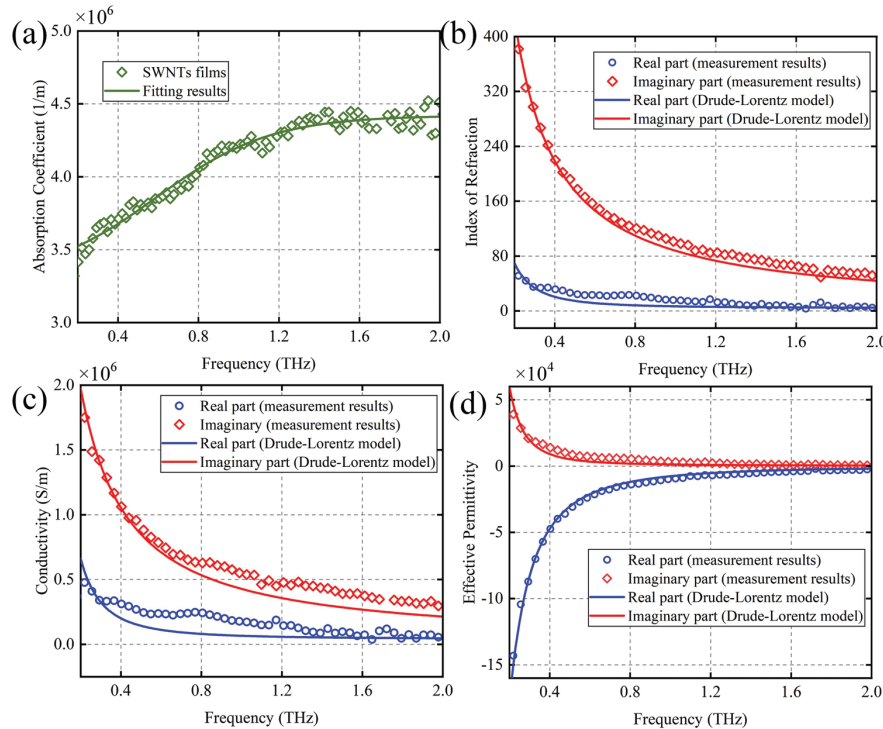


Figure 6. Comparison of the measured optical constants of SWCNTs film with theoretical results fitted by the D-L model. a) Absorption coefficient. b–d) The real and imaginary parts of the refractive index, conductivity, and dielectric constant, respectively. Reproduced with permission.^[132] Copyright 2022, Royal Society of Chemistry.

represents the fraction of a carrier's initial velocity that is retained after the n -th scattering events that allowing the D-L model to be generalized as:

$$\sigma_{DS}(\omega) = \sigma_D(\omega) \left[1 + \sum_{n=1}^{\infty} \frac{c_n}{(1 - i\omega/\gamma)^n} \right] \quad (16)$$

When scattering is elastic, the c_n is the expectation value $\langle \cos \theta \rangle$ where θ denotes the scattering angle θ . If scattering is completely isotropic Drude-like then $c_n = 0$, negative values of c_n imply a predominance of backscattering and for complete backscattering $c_n = -1$, while positive values of c_n denote a preponderance of forwarding scattering and for complete forward scattering $c_n = 1$. The value of n in Equation (16) is 1, which corresponds to the key assumption that persistence of velocity is retained for only one scattering. In particular, when $c_1 = -1$ and $c_{n>1} = 0$, the Lorentzian oscillator and D-S model gives an identical spectrum of conductivity upon the substitutions $\gamma_L = 2\gamma_D$ and $\omega_0 = \gamma_D$.

3.3. Effective Medium Theory

The network of crossed CNTs in the CNTs thin films contains both semiconducting and metallic nanotubes, which can be randomly distributed or orderly arranged depending on the preparation process. Also, the characteristic dimensions of the nanotubes are relatively small. Therefore, to better analyze the op-

tical constants of composites and hence predict their THz dynamic response, it is necessary to introduce the effective medium theory.^[140,141] Such theory gives the effective permittivity ϵ_{eff} of composite material in terms of the dielectric function ϵ_n of the nanotubes, and dielectric function ϵ_h of the host medium in which the nanotubes are embedded, and the volume fraction f ($0 < f < 1$) occupied by the nanotubes. The two most standard effective medium theories are the Maxwell-Garnett (M-G) and the Bruggeman effective medium theory, respectively, and whose basic physical properties have been well described by Aspnes.^[142] The optical parameters of both SWCNTs and MWCNTs have been successfully fitted by combining the M-G and D-L models, as shown in Figure 6.^[31,32,132,143,144] The M-G formula can be expressed as:^[145]

$$\frac{\epsilon_{\text{MG}} - \epsilon_h}{\epsilon_{\text{MG}} + 2\epsilon_h} = f \frac{\epsilon_n - \epsilon_h}{\epsilon_n + \epsilon_h} \quad (17)$$

If the CNTs films are composed of different chiral nanotubes with permittivity ϵ_n ($n = 1; 2; \dots; N$), then Equation (17) is generalized as:

$$\frac{\epsilon_{\text{MG}} - \epsilon_h}{\epsilon_{\text{MG}} + 2\epsilon_h} = \sum_{n=1}^N f_n \frac{\epsilon_n - \epsilon_h}{\epsilon_n + \epsilon_h} \quad (18)$$

where $\sum_{n=1}^N f_n = 1$, f_n represents the volume fraction of the n -th constituents of the complex medium. In general, best-fitting f parameters of M-G and D-L model for the CNTs films is 0.9.

In fact, there is always the existence of macroscopic percolating conduction channels for charge transport between nanotubes in CNTs films. In other words, CNTs films cannot be considered purely as a network of isolated nanotubes (or nanotube bundles) surrounded by air. Furthermore, it is difficult to determine which component is the host medium when the volume fraction f of the host medium to the filling medium is equal. Therefore, if the volume fractions of all components are comparable, the M-G theory is not applicable. The influence of geometry on inhomogeneous systems can be well described by the Bruggeman effective medium theory.^[146]

$$f_a \frac{\epsilon_a - \epsilon_{BG}}{\epsilon_a + 2\epsilon_{BG}} + f_b \frac{\epsilon_b - \epsilon_{BG}}{\epsilon_b + 2\epsilon_{BG}} = 0 \quad (19)$$

Here, a and b indicate that the two parts have different dielectric constants and filling fractions. Similar to the M-G formula, the generalized Bruggeman equation is written as:

$$\sum_{n=1}^N f_n \frac{\epsilon_n - \epsilon_{BG}}{\epsilon_n + 2\epsilon_{BG}} = 0 \quad (20)$$

Unlike isotropic unaligned CNTs film, the wafer-scale crystalline CNTs films of highly aligned and densely packed inherit the extremely anisotropic optical properties of individual CNTs on a macroscopic scale. The M-G and Bruggeman equations for anisotropic inclusions can be expressed:

$$\frac{(\epsilon_{MG})_p - \epsilon_h}{\epsilon_h + \nu_p [(\epsilon_{MG})_p - \epsilon_h]} = \sum_{n=1}^N f_n \frac{\epsilon_n - \epsilon_h}{\epsilon_h + \nu_p (\epsilon_n - \epsilon_h)} \quad (21)$$

And

$$\sum_{n=1}^N f_n \frac{\epsilon_n - (\epsilon_{BG})_p}{(\epsilon_{BG})_p + \nu_p [\epsilon_h - (\epsilon_{MG})_p]} = 0 \quad (22)$$

Here the numbers ν_p ($0 < \nu_p < 1$, $\nu_x + \nu_y + \nu_z = 1$) are the ellipsoid depolarization factors, and $p = x, y, z$ represent direction in space.

4. Application of CNTs-Based Optoelectronic Devices in THz and IR Frequency Band

In recent years, carbon-based low-dimensional nanomaterials, such as graphene and CNTs, have been considered as promising candidates for the development of next-generation photonic and optoelectronic devices working in THz and IR region due to their attractive electrical, optical and thermal properties.^[147–151] In particular, CNTs have some obvious advantages over traditional semiconductor materials such as Si and GaAs in terms of employment as light-emitting devices and photodetectors for on-chip or interchip optical interconnect.^[152–156] (i) CNTs are direct

bandgap semiconductors whose bandgap depends on the chirality index of the nanotubes. The intrinsic interband transitions of CNTs with different chirality can cover a wide wavelength range with specific luminous peaks, including the technically important communication band (1200 – 1550 nm); (ii) The nanoscale dimension of individual CNTs is very suitable for nanoscale light emitter in a nanophotonic circuit, which has the characteristics of low threshold voltage, simplicity, narrow spectral width, room temperature operation, very small volume, and good external drive; (iii) The intrinsic anisotropy of CNTs makes the highly ordered CNTs film a natural source and polarizer for emitting and detecting broadband polarized light; (iv) The one-dimensional nature of CNTs implies that electrons move in a ballistic transport way in the nanotubes, which in turn leads to ultra-high carrier mobility suitable for high-frequency photoelectronic devices including the THz and IR region;^[157,158] (v) Unlike semiconductor-based composite optoelectronic devices, CNTs can be fabricated directly on Si wafers. By integrating optical components such as emitter, detector, and modulator on a silicon chip, the on-chip, high-speed, and low-power optical communication is realized; (vi) The low-cost separation of high-purity single-chirality CNTs combined with the steady progress in the preparation technology of macroscopically highly aligned CNTs film has laid a solid foundation for the realization of highly integrated on-chip optoelectronics.

4.1. CNTs-based THz and IR Sources

THz and IR light sources are the basis for miscellaneous applications in environmental monitoring, industrial safety, astronomy, security inspection, optical communication, and sensing.^[159] The rapid development of semiconductor material and ultrafast optoelectronic technology has promoted and driven the development and application of a variety of THz sources, such as air plasma THz sources,^[160] nonlinear crystal THz sources,^[161] and photoconductive antenna (PCA) THz sources,^[162] which have been widely used in THz wave detection, spectroscopy, and imaging technology. The system of air plasma is complex and the spectrum is difficult to keep stable. The THz waves radiated by nonlinear crystals, such as inorganic semiconductor ZnTe, GaP, LiNO₃,^[163,164] organic semiconductor DAST (4-N,Ndimethylamino-4'-N'-methyl stilbazolium tosylate),^[165,166] OH1 (2-(3-(4-hydroxystyryl)-5,5-dimethylcyclohex-2-enylidene) malononitrile),^[167] and poled polymers,^[168] require accurate phase matching, thus their generation efficiency is low and the bandwidth is difficult to broaden. The PCA based on LT-GaAs (Gallium Arsenide grown at low temperature) and InGaAs can not only generate THz radiation but also be used to detect THz waves.^[169,170] However, the radiation power of THz waves from PCA still difficult to satisfy the requirements of high-power sources. In the IR frequency region, advanced light sources based on quantum cascade lasers and light-emitting diodes show fast modulation speed, but their high cost seriously hinders their use and promotion in practical applications.^[171,172] As such, the most common IR light source in conventional systems is the incandescent lamp which use an electrically heated filament to generate thermal emission. Traditional incandescent light sources emit light waves over a wide spectrum range and are limited to

modulation rates of about 10 Hz, leading to them being less than ideal for numerous applications.

An ideal light source should combine low cost, high efficiency, high stability, and high modulation rate that enables frequency-multiplexed detection schemes. CNTs-based emitter, as a kind of emerging broadband polarized light source, has recently captured extensive attention in both industry and research groups. Its preparation process is simple, only two metal electrodes are deposited on the CNTs film without the need to complex bandgap engineering through carrier doping and composition control, thus it is easy to obtain an emitter with a small footprint.^[152] On the one hand, CNTs films with large areas and high uniformity can well meet the requirements of amplifying the emitted light.^[154] On the other hand, the chirality separation of CNTs ensures that only one main peak appears in the electroluminescence (EL) and photoluminescence (PL) spectra, that is, ensuring the monochromatism of the light source.^[173] Most importantly, the natural linear polarized properties of parallel or vertically super-aligned CNTs films are of tremendous significance for good integration with waveguides and other optoelectronic devices.^[173–175]

According to luminescence mechanisms, CNTs-based light-emitting devices are typically classified into three categories: (i) EL devices;^[152–154] (ii) PL devices.^[158,176] The luminescence mechanism of these two devices is electron-hole recombination of exciton or free carrier generated electron-hole, but the former is electrically driven, and the latter is driven by light. (iii) thermal light emission devices, namely, joules heating CNTs to generate blackbody radiation.^[159,177–179] EL and PL can only be obtained from s-SWCNTs, whose emission spectra consist of a series of sharp 1D van Hove singularity peaks corresponding to the bandgap energy. EL and PL devices have the advantages of simple structure, stable luminescence, high efficiency, modulation rate up to GHz, and the ability to be compatible with functionally integrated optical circuits. However, direct fabrication or post-processing of high-purity or even single-chirality s-SWCNTs requires sophisticated equipment and strict processing technology, which limits the wafer-scale production of EL and PL devices to a certain extent. By contrast, m-CNTs, s-CNTs, or a mixture of both can be used for blackbody emission. Additionally, in contrast with EL and PL devices, the main advantages of CNTs-based black-body radiation devices are simple fabrication process, low cost, and ease to manufacture on a large scale. The disadvantage of thermal optical emission is that it can only radiate the broad spectrum described by Planck law, therefore it cannot obtain a monochromatic source. Owing to the wavelength dispersion of the light wave being large, rendering the potential communication speed past the optical waveguide is reduced.^[179]

In 2011, Muthee et al. demonstrated experimentally for the first time that electromagnetic waves in the THz region radiated from Joule-heated SWCNTs array film.^[179] The radiation resides in a broadband spectrum covering a frequency range of 1.2 THz, and the frequency can be tuned by adjusting the size of the CNTs-based THz antenna. In addition, the spectrum, radiation mode, and output power of these devices were studied in detail, and the total maximum radiated power was estimated to be 450 nW. Although the physical mechanism in the emission process is still unknown, this work undoubtedly opens a new way for the basic research of THz emission and detection based on SWC-

NTs. In the same year, Mikheev et al. experimentally observed the photon-drag effect in SWCNTs thin films.^[180] This phenomenon makes it possible to generate THz waves by using picosecond and femtosecond lasers to pump SWCNTs thin films. In 2014, Tatsuya et al. fabricated the first electrically driven, ultrahigh-speed (1–10 Gbps), compact footprint, and on-chip blackbody emitter based on unsuspended SWCNTs thin film that operates in the near IR frequency band,^[152] as shown in **Figure 7a**. The ultrafast temperature response, determined by the small heat capacity of the CNTs film and its high heat dissipation to the substrate, is responsible for the ultrafast response of these devices. Using this device, the researchers experimentally achieved pulse light generation with a width of 140 ps and real-time optical communication. Such CNTs-based light emitters fabricated directly on silicon substrates could be integrated into silicon-based optoelectronic circuits, and find various applications in fields such as integrated photonic and optical interconnects.

In 2015, Titova et al. demonstrated the emission of coherent broadband (0.2–2 THz) THz radiation from a macroscopically horizontally aligned, 2 μm thick SWCNTs array film excited by 400 or 800 nm femtosecond optical pulses in the absence of an externally applied bias, as shown in **Figure 7b**.^[158] The up-down asymmetry in the morphology of SWCNTs film induces a built-in electric field in s-SWCNTs that drives electron-hole pairs toward two ends of the nanotubes, thus generating transient THz pulses polarized along the nanotube axis. In 2016, Felix et al. proposed and demonstrated an electrically driven high-speed CNTs-based light source integrated onto a one-dimensional photonic crystal nanobeam cavity that enables remarkably narrow linewidth.^[153] The ultra-high quality factor of photonic crystals effectively eliminates the linewidth broadening arising from temperature, surface interaction and hot carrier injection, thus achieving on-resonance coupling efficiency above 75% and on-chip modulation rates in the GHz frequency range. These integratable, nanoscale photonic emitters with tailored optical properties will give rise to a surge of applications in optical communication, optical signal processing, on-chip sensing time-resolved spectroscopy, digitally controlled light sources, and so forth.

Compared with horizontally aligned SWCNTs, vertically aligned MWCNTs grown directly by the CVD technology have the obvious advantages of simple fabrication, low cost, and large-scale production, which is helpful to further realize the practical application of CNTs-based THz emitters. In 2018, Huang and colleagues observed and measured the generation of coherent, broadband (0.1–2.3 THz) THz signal from pure vertically aligned MWCNTs films grown on quartz substrate excited with a linearly polarized laser pulse at 800 nm, as illustrated in **Figure 7c**.^[181] The experimental results reveal that the linear dependence of the THz electric field on the pump power exhibit a typical second-order nonlinear optical effect for the THz generation process. They believe that the transient photocurrent for emitting THz pulses is mainly derived from the photon-drag effect in SWCNTs thin films. With the aim of elucidating the physical mechanism of THz generation, THz emission spawning from non-conductive polymer-coated vertically aligned MWCNTs composite material was implemented for comparison. The free carriers in the pure vertically aligned MWCNTs film can be transported both along a single nanotube and through the charge channel between adjacent nanotubes. Due to isolated carrier transport between

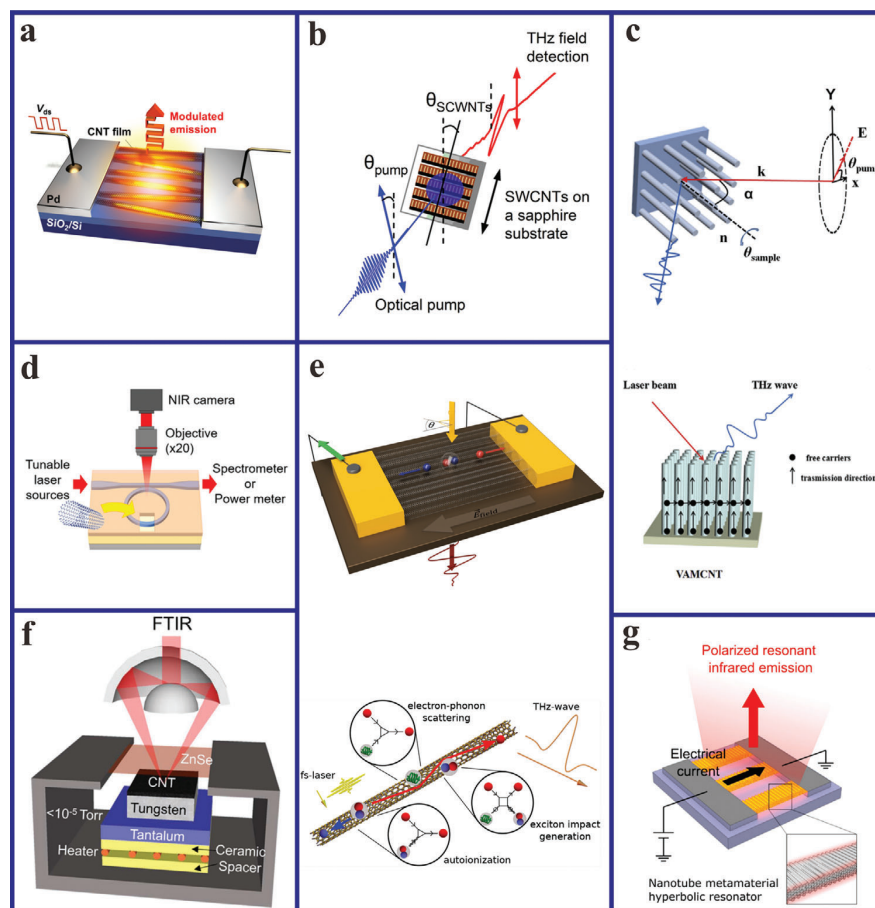


Figure 7. THz and IR emitter based on CNTs. a) An electrically driven CNTs light emitter lying on a SiO₂/Si substrate between two Pd electrodes. Reproduced with permission.^[152] Copyright 2014, American Chemical Society. b) Schematic drawing of THz radiation from aligned CNTs arrays excited by femtosecond optical pulses. Reproduced with permission.^[158] Copyright 2015, American Chemical Society. c) Top: Schematic illustration of VAMCNTs excited with polarized laser pulse in a reflection configuration. Bottom: Schematic illustration of the carrier transport channel in pure vertically aligned MWCNTs films. Reproduced with permission.^[181] Copyright 2018, Elsevier Ltd. d) Schematic drawing of an SWCNTs-silicon emitter with waveguides and microresonators. Reproduced with permission.^[182] Copyright 2020, American Chemical Society. e) Top: A CNTs-based THz PCA antenna. Bottom: Schematic diagram of exciton autoionization and multiplication for THz emission. Reproduced with permission.^[176] Copyright 2020, American Chemical Society. f) Schematic diagram of the experimental configuration of a CNTs-based mid-infrared hyperbolic thermal emitter. Reproduced with permission.^[178] Copyright 2014, American Chemical Society. g) Schematic illustration of polarized, spectrally selective mid-infrared thermal emission from a CNTs metamaterial hyperbolic nanoribbons resonator. Reproduced with permission.^[159] Copyright 2022, American Chemical Society.

adjacent nanotubes by the coated polymer, the free electrons and holes in the polymer-coated vertically aligned MWCNTs composite film are mainly transported to two ends of the nanotube along the nanotube axis. The different carrier transport mechanisms in the two types of CNTs films indicate that the emitted THz pulses from the composite film have a more regular THz response compared to that of the pure vertically aligned MWCNTs film, which is an open new route for the fabrication of vertically aligned MWCNTs-based THz emitters with stable performance.

In 2018, Liu et al. investigated the thermal radiation properties of intrinsic s- and m-SWCNTs suspended in the vacuum by continuous-wave laser heating.^[177] At 1000–2000 K high temperature, intrinsic s-SWCNTs emitted ultra-narrow linewidth IR radiation with linear polarization along the nanotube axis, with

respect to its broadband 1D metallic counterpart. The thermal excitation produces many excitons inside the s-SWCNTs, and the correlation between these excitons concentrates the oscillator strength into discrete energy levels, which causes the s-SWCNTs to radiate polarized ultra-narrow-band NIR light into free space. In 2020, Naoto et al. creatively integrated SWCNTs, microresonators, and waveguides on a silicon-on-insulator substrate to efficiently generate low-background, narrow linewidth, in-line PL at the 1.55 μm communication band under photoexcitation, as shown in Figure 7d.^[182] The ring or disk resonator is capable of confining light to extreme subwavelength-scale dimensions, leading to PL emission from SWCNTs being enhanced by a factor of approximately 34, with a maximum quality factor of 5700.

In 2020, Bagsican et al. developed a prototype dipole-type PCA antenna made from horizontally aligned, single-chirality (6,5) s-SWCNTs array film deposited on a sapphire substrate (Figure 7e top panel).^[176] The principle of the radiation THz pulse is shown in Figure 7e bottom panel, excitons in the SWCNTs film spontaneously dissociate into electrons and holes after the fs-laser excitation. Under low applied electric field, these free carriers are accelerated and radiate out high-intensity THz pulses, with promising emission efficiency only an order of magnitude lower than that of state-of-the-art LT-GaAs PCA switches. In addition, under high bias voltage, carrier multiplication occurs due to exciton impact generation, resulting in the PCA antenna operating in non-linear mode.

In 2019, Gao and co-workers introduced and successfully realized macroscopically ordered assemblies, or crystals, of CNTs as a remarkable refractory material platform for hyperbolic thermal emitters in the mid-infrared spectrum range, as depicted in Figure 7f.^[178] In direct thermal emission measurements, strongly polarized, broadly tunable, narrow-band, and spectrally selective thermal emissions from wafer-scale crystalline films of highly aligned SWCNTs are observed at 700 °C operating temperature. The photon-like resonance in an indefinite cavity with a volume smaller than $\lambda^3/700$, where λ is the resonance wavelength, manifests that the ultra-high thermal photonic density in the macroscopically aligned SWCNTs film is at least 100 times greater than that in the blackbody emitter. In 2022, John et al. present and fabricate an on-chip electrically driven, spectrally selective thermal emission light source based on globally aligned and densely packed CNTs film prepared via spontaneous alignment that occurs during the vacuum filtration process.^[159] In Figure 7g, the self-assembled CNTs films are cut into nanoscale ribbons to function both as refractory hyperbolic resonators and as heating elements. By designing the optical resonator geometry, the radiation wavelength can be tuned over a broadband spectrum range, imparting spectral selectivity to the thermal emitter. Benefiting from the nanoscale heated volume and short thermal time constant of CNTs film, this device yielded a maximum modulation rate of 1 MHz, which is several orders of magnitude higher than that of standard incandescent lamps.

4.2. CNTs-Based THz and IR Modulators

Modulator refers to a device that manipulates one or more characteristic parameters of electromagnetic wave, including amplitude, frequency, phase or polarization. It is widely used in communication, polarization imaging, spectroscopy, sensing and other fields.^[20,183–185] To achieve the manipulation of IR and THz radiation, novel THz and IR modulators fabricated from a variety of materials have been extensively explored. These materials include semiconductors,^[186] metamaterials or metasurface,^[187,188] photonic crystals,^[189] phase change materials,^[190–192] liquid crystals,^[193–195] perovskites,^[196,197] transparent conductive oxides,^[198,199] and two-dimensional materials.^[200–202] IR and THz modulators have made impressive progress over the past two decades, but the commercialization of fast-speed, efficient, and miniaturized modulators ranging from THz or IR band still stands in its early stages compared to the

currently available massive commercial THz and IR sources and detectors.

CNTs exhibit very attractive advantages in the preparation of THz and IR passive or active modulator, especially polarizers. For example: (i) simple, rapid, and reliable fabrication. The fabrication of CNTs-based polarizers does not require complex processes such as electron beam lithography and chemical etching;^[203] (ii) CNTs have high intrinsic optical anisotropy due to their unique one-dimensional nanostructure, which can be used as polarizers to realize transmission or absorption of linearly polarized electromagnetic waves in different polarization directions;^[204] (iii) The extinction ratio and polarization degree of THz polarizers based on CNTs can be dynamic adjusted freely by controlling the number of layers of CNTs film; (iv) CNTs can respond to ultra-wideband light from THz to ultraviolet (UV) range, therefore, CNTs-based polarizers operate in the wideband region and have small dispersion; (v) At present, a CNTs-based THz polarizer with an extinction ratio of 37 dB has been reported, which is comparable to the highest value obtained by the most advanced commercial wire-grid polarizer, thus can well meet the requirements of practical applications;^[203] (vi) The thermal stability, mechanical robustness, and chemical stability of CNTs ensure semi-permanent employment of the device; (vii) The size of the polarizer, that is, the size of the CNTs film, can be tuned freely and the thicker film can be easily produced; (viii) The characteristics of CNTs films can be modified by means of electric bias, carrier doping, etc., which means the potential in the fabrication of active THz and IR modulators. Owing to these advantages, CNTs represents a high-performance material that can penetrate the next-generation novel THz polarizer market in the near future.

In 2009, Ren et al. first presented THz linear polarizers fabricated from SWCNTs thin films, and anisotropic THz absorption resulted from the intrinsic optical anisotropy of the macroscopic thin films endowed by the extremely high horizontal alignment of the nanotubes (Figure 8a).^[205] The device exhibits 80% degree of polarization (DOP) and extinction ratio (ER) of 10 dB under THz wave irradiation in the broadband range of 0.1–1.8 THz. The authors predicted that the performance of the THz polarizer could be effectively improved by simply increasing the thickness of the CNTs film. In 2012, they increase the effective film thickness by continuously stacking the aligned SWCNTs films (Figure 8b), thus achieving an advanced THz polarizer with remarkable 99.9% DOP and ER up to 35 dB over a wide spectral range of 0.1 to 2.0 THz.^[204]

In a parallel effort, Kyoung et al. fabricated micrometer-thick free-standing THz linear polarizer by mechanically winding highly oriented MWCNTs aerogel sheet on a U-shaped polyethylene frame, as shown in Figure 8c.^[203] This novel approach can easily control the orientation and thickness of MWCNTs films at the same time and has good potential for commercial application. A 75-layer MWCNTs sheet (9 μm thick) is used as a linear polarizer. Over most of spectral range (0.1–2.0 THz), The devices showed an ideal DOP close to 99.9% with giant ER of ≈ 37 dB. In addition, the researchers compared the polarizer fabricated in such a way with a commercial wire-gate polarizer and demonstrated that the performance of CNTs-based polarizer outperformed the commercial product.

In 2017, a scalable cost-effective strategy to produce three-dimension architectures of aligned and modulation-doped

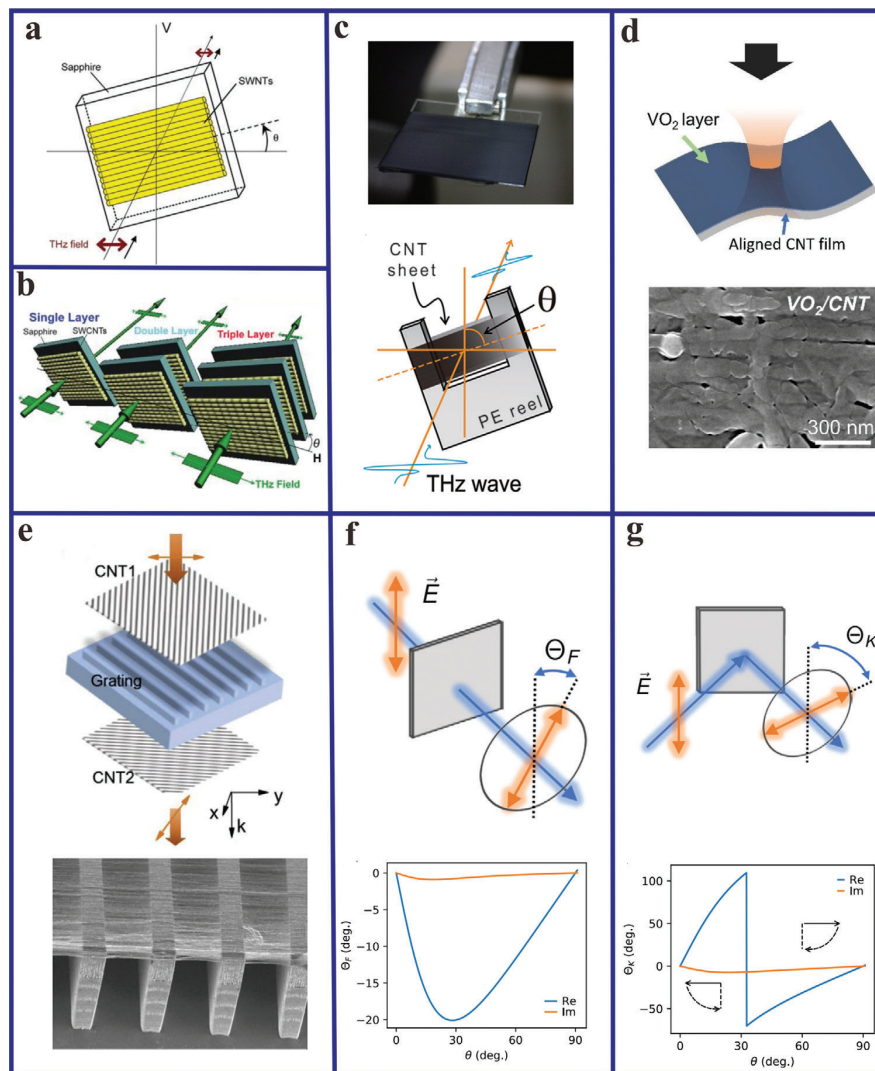


Figure 8. Various CNTs-based THz and IR modulator. a) The experimental scheme of THz transmission measurements for the highly horizontally arranged SWCNTs thin film. Reproduced with permission.^[205] Copyright 2009, American Chemical Society. b) A high-performance THz polarizer built with stacks of aligned SWCNTs films. Reproduced with permission.^[204] Copyright 2012, American Chemical Society. c) Top: Photographic images of A 75-layer CNTs-based polarizer. Bottom: Sketch of the experimental configuration for the polarization state measurements. Reproduced with permission.^[203] Copyright 2011, American Chemical Society. d) Top: Schematic of the architecture of a VO₂/CNTs active THz amplitude modulator. Bottom: An enlarged scanning electron microscopy (SEM) image of the aligned VO₂/CNTs film. Reproduced with permission.^[210] Copyright 2020, Royal Society of Chemistry. e) Top: Schematic representation of a THz polarization convertor integrating a subwavelength dielectric grating and CNTs sheet. Reproduced with permission.^[215] Copyright 2018, Elsevier Ltd. A SEM image of CNTs/grating polarization convertor. Giant polarization rotations by THz transmission f) and reflection g) through the super-aligned SWCNTs film. Reproduced with permission.^[217] Copyright 2021, OSA Publishing.

SWCNTs with long-term stability is demonstrated, in which multiple thin (20 nm) layers of highly aligned, densely packed SWCNTs films with dopants inserted between the layers.^[206] This modulation-doped, multiple-quantum-well structure functions as a THz and IR polarization device and exhibit an ultra-broadband operating frequency range (from 0.2 to 200 THz) with a consistently high ER of 20 dB in the THz band (from 0.2 to 1 THz) and extremely low insertion loss value of less than 2.5 dB in the whole spectral range, and the overall performance sur-

passes that of previously reported CNTs-based THz polarizers. This stacking and doping fabrication procedure is general and can in principle be extended with no limitations in size and thickness, which will address a fundamental challenge in the development of THz optical devices.

The aforementioned CNTs-based THz polarizers are all static types, and static THz polarizers cannot provide fast enough exchange speeds to fully exploit the potential of THz communications. Dynamic THz polarization has been observed on highly

aligned s-SWCNTs during photoexcitation, which may offer a scheme for the fabrication of active THz polarizers. Based on this concept, in 2014, Docherty et al. studied ultrafast dynamic modulation of THz radiation by unaligned optically pumped narrow chirality distribution of s-SWCNTs.^[207] Selective photoexcitation of the (7,5) s-SWCNTs by a polarization-controlled optical pump induces transient and tunable THz polarization. The transient polarization of THz radiation decays within picoseconds scales, thus allowing the polarizer to modulate THz waves on subpicosecond timescales. The device exhibits an amplitude modulation depth of -27 dB and the modulation performance can be enhanced by increasing the density of nanotubes in the sample or by stacking the layers of the CNTs sample.

As a phase change material, vanadium dioxide (VO₂) is almost transparent in the THz frequency band in the insulating phase, while the great increase of carrier density in the metallic phase makes it show a strong response to the incident THz wave. Therefore, VO₂ attracts growing attention act as an active THz modulation material. Several recent studies have shown that textured VO₂ can be grown well on CNTs films by coating or deposition under appropriate conditions.^[208,209] On the basis of progress of preparation technology, in 2020, Ma et al. develop a flexible, active THz amplitude modulator made of VO₂ deposited on aligned CNTs thin film, as shown in Figure 8d.^[210] THz wave modulation driven by drastic, reversible metal-insulator phase transition of VO₂ shows a large amplitude modulation depth as high as 91% (10.4 dB) in broad frequency ranging from 0.2 to 2.5 THz, combined with short response time of 27 ms, low triggering threshold of 0.58 mW mm⁻² and low insertion loss, demonstrating the remarkable utility of aligned CNTs films coated with VO₂ for emerging THz applications.

Traditional THz polarization converters mainly take advantage of the natural birefringence of uniaxial crystals, but their performance is limited by the shortcomings of large size, large volume, and high loss.^[211,212] Artificial electromagnetic metamaterials or metasurface can achieve efficient polarization rotation and conversion of THz waves at large bandwidths by introducing artificial mode birefringence or chiral polarization rotation.^[213–215] Compared with natural birefringent crystals, metamaterials have the prominent advantage of ultrathin dimension, easy to integrate, and flexible in design, but their fabrication is typically realized based on expensive and complex methodologies. In 2018, Xu et al. developed a THz linear polarization converter by combining two orthogonal films of highly aligned CNTs with a subwavelength dielectric grating, as illustrated in Figure 8e.^[215] Due to the subwavelength integration and presence of cavity mode, local electromagnetic resonance is generated between the two CNTs films and subwavelength dielectric grating, which greatly enhances the polarization rotation and enlarges the bandwidth. The performance of THz linear polarization converter, such as phase-shift dispersion and impedance, can be controlled by adjusting the number of layers of the CNTs film, and the broadband near-zero dispersion throughout a frequency range of 0.4–0.95 THz has been finally obtained. In 2021, they further fabricated a multi-band THz linear polarization converter consisting of the CNTs films sandwiched by two sub-wavelength metal grating.^[216] In this architecture, CNTs sheet act as polarizers and metal gratings are used as artificial wave plates due to large birefringence. The perfect orthogonal polarization conversion has

been achieved due to the multi-layer polarization selection and multiple reflections in the microcavity constructed between the carbon nanotubes sheet and the metal grating. In the same year, Baydin et al. demonstrated a THz polarization device built with ultrathin, high-density, wafer-scale crystalline, aligned SWCNTs films exhibiting giant THz properties: the transmission THz polarization rotation can reach ≈20° and the reflection can reach ≈110°, respectively (Figure 8f,g).^[217] These giant THz rotations are a result of the extreme birefringence of super-aligned SWCNTs films arising from extremely anisotropic optical constants of single SWCNTs.

4.3. CNTs-Based THz and IR Photodetectors

Photodetectors that are sensitive to THz to IR electromagnetic radiation lay the foundation for diversified applications in astronomy, spectroscopy, remote sensing, high-resolution imaging, non-invasive inspection, material characterization, and optical communications.^[218–226] CNTs are not only outstanding THz and IR emitters, but also promise some strong advantages for the next-generation high-performance and energy-efficient photodetectors in terms of ultrahigh charge carrier mobility, superior photoresponse, simplified growth and device fabrication, long exciton diffusion length, good mechanical flexibility, and room-temperature operation.^[227–229] Also, the multiple exciton generation and multiphoton absorption of carriers in SWCNTs further offer the potential for promoting the detection efficiency of CNTs-based photoelectric devices.^[230] Additionally, CNTs aggregations (chirality-mixed arrays or films) are capable of absorbing a wide scope of electromagnetic radiation ranging from UV to THz through both the intraband transition and the interband transition absorption mechanisms,^[227] which makes it possible to achieve ultra-wideband CNTs-based detectors. According to the fundamental photo-response mechanism for detecting THz and IR radiation, one classifies CNTs-based photodetectors into two major categories, namely, photonic detectors (for example photoconductors, phototransistors, and photodiodes) and thermal detectors (such as bolometers, photothermopile). Thermal detection has the advantage of wide spectrum bandwidth and simple structure but at the cost of response speed and sensitivity. By contrast, photonic detectors are characterized by fast response speed and high sensitivity, but they suffer from a dramatic response cutoff when the photon energy is less than the bandgap energy, leading to limited bandwidth.

4.3.1. Thermal Detectors

A THz and IR bolometer, also referred to as bolometric THz and IR sensor, is a thermally isolated thin device that absorbs THz and IR electromagnetic radiation and converts this to the increase in temperature of the active material leading to a change in its resistance.^[231] Since the performance of the bolometer depends mainly on the resistance variation, materials with low specific heat capacity and large temperature coefficient of resistance become the primary candidates for the preparation of the bolometer. CNTs have unique advantages in the development of high-performance bolometers for their tiny size, low specific heat

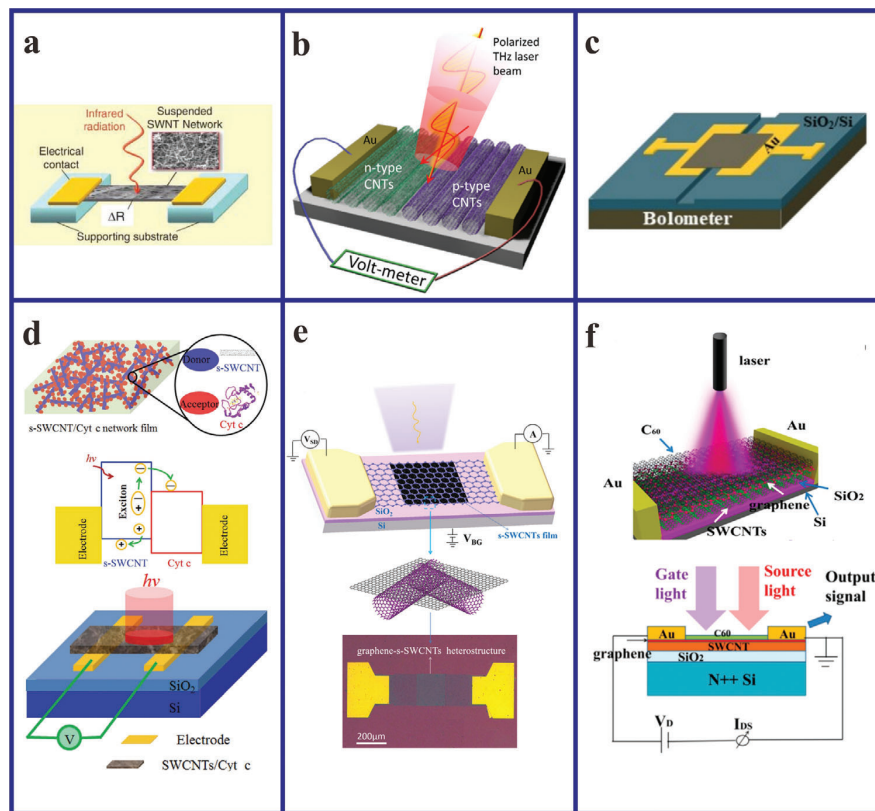


Figure 9. Various CNTs-based photodetectors in THz and IR bands. a) Schematic diagram of SWCNTs network suspended between electrical contacts. Reproduced with permission.^[232] Copyright 2006, American Association for the Advancement of Science. b) A polarization-sensitive THz detector composed of p-type and n-type aligned CNTs array film. Reproduced with permission.^[241] Copyright 2014, American Chemical Society. c) A suspended bolometer of VO₂-coated MWCNTs film. Reproduced with permission.^[244] Copyright 2019, American Chemical Society. d) Schematic of the s-SWCNTs/Cyt c nanohybrid films (top) and the band-edge offset across the s-SWCNTs/Cyt c interface (middle) for exciton dissociation. Bottom: Schematic of the s-SWCNTs/Cyt c nanohybrid films device and the test circuit. Reproduced with permission.^[246] Copyright 2015, Springer Nature. e) Top: A graphene-s-SWCNTs heterostructure photodetector on SiO₂/Si substrate with two electrodes. Bottom: Optical image of the as-fabricated photodetector. Reproduced with permission.^[256] Copyright 2018, American Institute of Physics. f) Top: The planar structure of SWCNTs/graphene/C₆₀ heterojunction. Bottom: Schematic illustration of the all-carbon photodetector based on SWCNTs/graphene/C₆₀ heterojunction. Reproduced with permission.^[223] Copyright 2020, American Chemical Society.

capacity, high THz and IR infrared absorption, and prominent high-temperature stability. In 2006, Haddon and co-workers experimentally demonstrated a highly sensitive IR bolometer made of the SWCNTs film suspended between two electrical contacts in the vacuum, as illustrated in **Figure 9a**.^[232] At a low temperature of about 50 K, the photoresponse of the suspended SWCNTs film shows a resistance decrease of 0.7%, with a response time of 50 ms under IR radiation. In a controlled experiment, the CNTs film supported directly on the substrate exhibited no detectable change of resistance. After reducing the thickness of the film to 40 nm and removing the m-SWCNTs in the film the resistance temperature coefficient (TCR) of the film increases from 1 to 2.5% over the entire temperature range, which results in a recorded responsiveness of 1000 V/W and the noise power density of less than 10⁻¹⁴ V²/Hz.

Owing to the higher heat generation of the CNTs network and higher temperature gradient of resistivity of the polymer matrix, the performance of the CNTs film bolometer can be substantially

improved by embedding SWCNTs into an electrically and thermally insulating polymer matrix. A variety of non-conductive polymers have been widely used to enhance the activation energy of CNTs films, including but not limited to polycarbonate,^[233] polystyrene,^[234] polyaniline,^[235] poly(3-octylthiophene),^[236] poly(N-isopropylacrylamide),^[237] poly(3-hexylthiophene)-block-polystyrene.^[238,239] In 2013, Xu et al. obtained the largest TCR observed to date, -10%/K, from CNTs-polymer nanocomposites prepared by incorporating SWCNTs into a non-conductive phase-change hydrogel poly(N-isopropylacrylamide),^[237] even larger than that (3%/K) of vanadium oxide, the leading active material for the preparation of uncooled bolometer. At the critical temperature of poly(N-isopropylacrylamide), it undergoes a volumetric phase transition, resulting in a significant change in dielectric constant, which in turn greatly enhances the activation energy required for electrons tunneling between CNTs and thus increases the temperature dependence of the resistivity. In a parallel effort, Gustavo and co-workers prepared and characterized

the photothermoelectric properties of densely packed and highly aligned films of horizontally aligned SWCNTs in a polymer matrix in order to evaluate their potential as bolometers.^[240] The average values obtained for bolometric response times and TCR of the SWCNTs bolometers are 420 μ s and $-2.94\%/K$, respectively. The maximum voltage responsivity of 230 V/W along with detectivity of 1.22×10^8 cm Hz^{1/2}/W was measured. These values clearly indicate that dense networks of horizontally aligned SWNTs are responsible for their exceptional bolometric properties.

The aligned SWCNTs films inherit the strong optical polarization sensitivity of individual nanotubes, which offer a promising potential for polarization-sensitive detectors in applications including communication, navigation, astronomy, material and surface orientation, remote sensing, and enhanced scene. He et al. developed a photothermoelectric p-n junction photodetector with intrinsic broadband polarimetry based on two macroscopic films of horizontally aligned and ultralong doped SWCNTs, consisting of a mixture of semiconducting and metallic SWCNTs (Figure 9b).^[241] Strong polarization ratios up to $\sim 5:1$ and responsivity as high as ≈ 2.5 V/W at 2.3 THz are achieved in this detector, and the broadband spectral response extends from the visible to the MIR and even the THz regime. The consistency of experimental and theoretical results unambiguously reveals that the photoresponse mechanism of the device is dominated by the Seebeck effect. The performance of self-powered, broadband, flexible, polarization-sensitive CNTs-based photothermoelectric detectors that operate at room temperature will undoubtedly be substantially improved and optimized by further tailoring CNTs thermoelectric properties.

MWCNTs can be thought of as a coaxial cylinder of graphene composed of a group of metallic and semiconducting SWCNTs shells. This nested unique structure enhances the absorption ability of nanotubes to incident radiation to a large extent, which is proportional to the number of inner shells. At the same time, the outmost shell (or few shells) of MWCNTs isolates the thermal link between the inner shell and the external environment, thus potentially improving the sensitivity of the detector. In addition, from the perspective of sample preparation, it is easier to prepare high-yield, densely aligned, and uniformly thick MWCNTs films, which in turn may lead to high IR and THz bolometric photoresponse.^[242] In 2010, Wu and coworkers developed a high-performance bolometers based on MWCNTs films suspended onto patterned SiO₂/Si substrate with a 500 nm thick thermal oxide layer.^[243] They observed the enhanced detectivity of 3.3×10^6 cm Hz^{1/2}/W by a factor of 7 as compared to SWCNTs counterparts. Also, the MWCNTs bolometer revealed a short response time of around 1–2 ms, which is more than an order of magnitude shorter than that obtained on the SWCNTs bolometer. The enhanced bolometric performance in the suspended MWCNTs film was mainly attributed to high photon absorption per tube and reduced thermal link to the environment provided by the naturally suspended inner shells structure in MWCNT. In 2019, Sukanta and Abha reported a coating and transfer method to fabricate a freestanding bolometer of vanadium oxide-coated MWCNTs (Figure 9c).^[244] The main reasons behind vanadium oxide being chosen consist in its large TCR, ranging from ≈ 2 to 5%/K, and low 1/f noise. Due to the synergistic effect between vanadium oxide and MWCNTs with unique microscopic configurations,

the fabricated detectors exhibit a TCR value of approximately 486% higher than the absolute TCR value reported free-standing MWCNTs at room temperature and voltage responsivity in exceeding 67 V W⁻¹ at 200K for 50 ms⁻¹ modulation frequency. This work opens up a new opportunity for developing highly-sensitive, high-performing, large-area, suspended MWCNTs film photodetectors that operate at room temperature.

The natural nanoscale dimensions of SWCNTs also endows its flexibility in embedding other photonic or hybrid optoelectronic systems. In 2016, Peng's group presented the first microcavity-integrated diode-type CNTs photodetectors by monolithically integrating single-nanotube into a designed planar Fabry–Perot microcavity.^[224] In this work, they elucidated the mechanisms associated with cavity-integrated devices and observed a 6-fold increase in photoelectric conversion efficiency as compared with results from a single-tube device in free space. Additionally, by employing chirality-enriched semiconducting (8,3) and (8,4) CNTs as active materials, whose band-gap energy overlaps with the resonant mode of the designed cavity, the recognition of a specific target signal among a broad background of signals or noise was also achieved. Under optical-mode-allowed resonance excitation, the cavity-integrated film photodetector showed an enhanced suppression ratio until a power density of 0.07 W cm⁻² and photocurrent of 5 pA, and a narrower spectral full width at half-maximum is 33 nm at a target signal wavelength of 1200 nm. This study provides a promising and practical pathway for developing chirality-specific CNTs film-based signal detection and recognition systems for information optoelectronics on a chip.

Inkjet printing has emerged as a promising approach for fabricating large-area, high-throughput, and low-cost optoelectronic device and is particularly suitable for THz detectors since detector size requirements are greater than the operating wavelength. In 2020, Llinas et al. developed a photothermoelectric THz detector constructed by inkjet printing of aqueous CNTs inks on sub-micrometer thick, ultra-flexible poly ethylene terephthalate.^[245] They exploited the doping properties of CNTs to prepare p- and n-type CNTs inks and thus realized optically thick p-n junction devices. Using this device, they demonstrated room-temperature noise-equivalent power (NEP) of 25 nW/Hz^{1/2} at 3.8 THz with no voltage bias, enabling antenna-free single-pixels for THz transmission imaging. For the purpose of improved photoelectric response, they also developed a 3D folding of detector pixels based on origami architectures with NEP to up 12 nW/Hz^{1/2}, close to the NEP of existing THz detectors assembled with filtered CNTs films.

Arrays of vertically aligned, densely packed SWCNTs (SWCNTs forest) behave nearly unity black-body absorption characteristics with a near-perfect absorptance of 0.98–0.99 over an ultra-broad spectral range from UV (200 nm) to THz (200 μ m), which can be explained as homogeneous sparseness and slightly tilted alignment of the SWCNTs within the forest. Due to the black body being capable of converting light to heat efficiently, it is of great significance in the applications such as energy harvesters, stay light shields, and infrared thermal detectors. In 2019, Yeow et al. developed a room-temperature, self-powered, large-area, compact, and broadband IR and THz photothermoelectric photodetector fabricated by a densely packed CNTs forest. An array of vertically aligned, densely packed CNTs is sandwiched by two conductive layers mounted on a Si substrate.^[218] By virtue of the

vertical photothermoelectric effect in an anti-reflecting CNTs forest, the device has achieved enhanced broadband photoresponsivity of 5.3 V/W with detectivity of $1.9 \times 10^7 \text{ Hz}^{1/2} \text{ W}^{-1}$ under weak and unfocused IR light. Surprisingly, peak responsivity up to 640 V/W and $2.3 \times 10^9 \text{ Hz}^{1/2} \text{ W}^{-1}$ at 4.3 THz was observed, which is attributed by the authors to enhanced light absorption induced by confined collective motion of carriers in the tube-length scale and weak hot-carrier relaxation. By further designing and constructing periodic ring-shape patterns in the top conductive layer to reduce reflection, they found that the photodetectivity at a wavelength range of 2.5–25 μm was enhanced by a factor of 6 in comparison with the non-patterns case, verifying that the performance of photodetectors can be effectively improved by integrating patterned conductive layers on densely packed CNTs forest.

4.3.2. Photonic Detectors

The binding energy of excitons in the semiconducting SWCNTs is the order of a few hundred meV,^[228,246] which reduces the yield of photogenerated free electrons and holes, thus achieving an efficient exciton dissociation mechanism that is a significant opportunity to develop high-performance photonic CNTs-based photodetectors. To shed some light on this long-standing problem, the formation of SWCNTs heterojunctions has been extensively applied to improve the exciton dissociation and charge transfer by combining various materials, for example, bulk semiconductors, low-dimensional nanostructures, biological molecules, and polymers. In 2012, Lu and co-workers demonstrated a standout photocurrent at type-II heterojunction formed by an interface between high-purity (~98%) s-SWCNTs and conjugated semiconductor poly (3-hexylthiophene),^[239] which results in enhanced figure-of-merit detectivity of $2.3 \times 10^8 \text{ cm Hz/W}^{1/2}$, and a small response time of 1 ms. Although these results are inspiring, the external quantum efficiency (EQE) of these devices is below 2% because the concentration of CNTs in Poly(3-hexylthiophene) cannot exceed 3% in order to maintain well-dispersed SWCNTs in the polymer. Based on this work, the same group further developed a room-temperature s-SWCNTs/ biomolecule cytochrome c (Cyt c) nanohybrid IR detectors with high photoresponsivity as much as 0.77 A/W and extraordinary EQE beyond 90% to NIR light (Figure 9d).^[246] In recent work, for the first time, they obtained the complete and detailed band structure and photoelectric properties of s-SWCNTs/Cyt c heterojunction interface through first-principles calculations. The calculated result predicts the band edge alignment across the s-SWCNTs/Cyt c heterojunction interface,^[247,248] thus forming a built-in electrical field up to 1.1 eV, which facilitates high-efficiency exciton dissociation and charge carrier transfer. By optimizing and engineering these devices, the remarkable EQE of $5.9 \times 10^4\%$, the saturated responsivity of 46 A/W, and detectivity as high as $10^{10} \text{ cm Hz/W}^{1/2}$ in the uncooled NIR detection were observed, which is attributed to the number of carriers collected per photoinduced carrier generated at the s-SWCNTs/Cyt c heterojunction interface. In the same period, a highly sensitive, self-powered, broadband photodetector composed of (6, 5)-enriched s-SWCNTs film/n-type GaAs Van der Waals heterojunctions was reported by Su et al.,^[249] showing that the formation of heterojunction could

substantially enhance the separation efficiency of the exciton. This device exhibits a photoresponsivity of about 274 mA/W and detectivity greater than on the order of $10^{12} \text{ Hz/W}^{1/2}$ with a response recovery time as low as 0.27 ms, which gives rise to extensive research interests in developing SWCNTs/bulk semiconductor van der Waals heterojunctions for photodetectors and solar cells.

Carbon allotropes have attracted a great deal of attention in photoelectric applications, including 0D fullerene (C_{60}), 1D SWCNTs, and 2D graphene, derive from their unique and superior chemical and physical properties. Combining various low-dimensional nanocarbon materials together to form all-carbon nanohybrids promises a prospective scheme to achieve the photonic and electronic devices operating with a novel principle. Tung et al. demonstrated that the CNTs chirality determines the efficiency of electron transfer from SWCNTs to fullerenes in all-carbon photovoltaic devices.^[250] Efficient charge transfer was identified by Yang et al. in the heterojunction formed between graphene and SWCNTs.^[251]

In addition, both theoretical and experimental results have shown that exciton dissociation is the most efficient when C_{60} is combined with SWCNTs compared with other materials.^[252–254] Park in collaboration with Lee et al reported an experimentally fabricated s-SWCNTs/ C_{60} -based phototransistor, where the C_{60} serves as electron traps that accept the photogenerated electrons from the SWCNTs.^[255] Upon IR illumination, they observed a linear increase in responsivity with tuning gate voltage, reaching a maximum value of 97.5 A/W at gate voltage of –2 V. Moreover, owing to the enhanced photoconductive gain of 20 000–40 000 electrons per photon in a s-SWCNTs/ C_{60} hybrid film, a high detectivity of $1.17 \times 10^9 \text{ cm Hz}^{-1/2} \text{ W}^{-1}$ was achieved at 1 kHz.

Apart from 0D C_{60} , 2D graphene has also stimulated theoretical and experimental study on CNTs/graphene hybrid nanostructures due to exceedingly high carrier mobility, excellent electrical conductivity, and thermal conductivity. In 2018, Cao et al. developed a high-efficient broadband photodetector based on a stacked heterostructure of CNTs/graphene, as shown in Figure 9e.^[256] Benefiting from the ultra-high photoconductive gain up to 8×10^4 , the device exhibits ultra-fast response time of 80 μs and relatively high responsivity of 78 A/W outperforming either graphene-based heterostructure photodetector. In 2020, Zhou et al. presented and analyzed the photoelectric performance of an all-carbon-based photodetector composed of a SWCNTs/graphene/ C_{60} heterojunction (Figure 9f).^[223] Graphene functions as the channel of charge transfer due to the highest mobility and relatively low absorbance of a single sheet of carbon atoms among the three kinds of carbon allotropes. Subsequently, utilizing SWCNTs and C_{60} as active layer that strongly responds to a broad spectrum ranging from visible to IR region. The photodetector exhibits a maximum photoresponsivity of 10 579 A/W in the visible region and a 545.7 A/W maximum response in the IR region (808 nm), which is correlated with the ultra-high EQE beyond on the order of $10^6\%$. Thanks to the high photoconductive gain, high responsivities, fast operating speeds, broad bandwidth, and high stable quality of all-carbon hybrid nanostructures, these devices afford a new opportunity toward high-performance, low-cost and scalable CNTs-based IR and THz detectors.

4.4. CNTs-Based THz and IR Perfect Absorbers

Broadband, omnidirectional, polarization-insensitive, and scalable absorbers in THz and IR regions have a wide range of applications in sensing/imaging, detection, modulation, receiving, and electromagnetic shielding to energy harvesting.^[257–261] Over the last decade, tremendous efforts have been witnessed to develop compact and high-performance THz and IR absorbers.^[262,263] However, most conventional materials exhibit zero reflection and complete light absorption only in certain frequency bands, not enough to cover the entire THz to IR spectrum, thus limiting their practical applications for controlling THz and IR waves. According to the absorption mechanism, perfect absorbers are mainly divided into resonant and non-resonant types.^[261,264] Resonance absorbers, such as metamaterial absorbers, achieve impedance matching at the interface between medium and air by carefully designing the subwavelength unit cell structure and producing near unity power absorbance but relatively narrow absorption peaks at the resonance frequency.^[260,264] In order to obtain the broadband spectrum, the strategy of superposition of multiple elements or multilayer metamaterials to hybridize the designed resonant frequencies is also proposed.^[265,266] These ultrathin metamaterial absorbers have the advantages of flexible design and tailored spectra, but often require sophisticated preparation procedures that severely hinder their further practical application. Non-resonant absorbers take advantage of the refractive index gradient formed in nanostructures and the enhanced multiple internal total reflections to obtain a wider absorption spectrum and can be prepared by simple and scalable methods.^[267,268]

The confinement of electrons along the CNTs axial direction gives rise to intriguing effects on their optical properties. For example, multiple pronounced, finite-frequency peaks in the UV to THz absorption spectrum have been universally observed in diverse types of SWCNTs samples. The origin of the UV absorption has been identified as the collective interband excitation of the π -band electrons caused by the absorption of linearly polarized light parallel to the axis of the nanotube.^[269] It is widely accepted that conspicuous absorption features in the visible and near-IR spectrum are derived from direct interband absorption that occurs across the bandgap.^[269–271] In contrast, plasmon excitation in m- and s-SWCNTs of finite tube length is responsible for the optical response in the THz to mid-IR region. In particular, the refractive index of vertically aligned CNTs (VACNTs) is very close to that of air, resulting in very low reflectivity at the interface between air and CNTs films. Hence, VACNTs resemble a black body in the broad spectral range from THz to UV, exhibiting extremely high absorption (more than 99.95%) of incoming electromagnetic waves in these frequency bands.^[272,273] Combined with the mechanical flexibility of CNTs, VACNTs are naturally suitable for the preparation of flexible, broadband THz and IR perfect absorbers.

In 2019, Sun et al reported the design, fabrication, and experimental demonstration of a wafer-scale VACNTs array with near-perfect absorption in the broadband range, as shown in Figure 10a.^[272] A VACNTs array composed of the CNTs with an average length of 600 nm is fabricated upon a 4 inches low-resistivity silicon through a thermal CVD deposition system. the complex refractive index of VACNTs array with different volume

fraction and volume fraction are investigated in the THz and IR regions employing the M-G efficient medium theory, revealing that the length, volume fraction, and orientation of the nanotube in the VACNTs array play an important role in achieving high and broadband THz absorption. Both the transmission and reflection measurement of the fabricated VACNTs array using the THz-TDS system shows that the average power absorbance of the absorber is as high as 98% in the frequency ranging from 0.3 to 2.5 THz, with average electromagnetic shielding effectiveness of 61 dB. This work provides a new approach for the development of novel, cost-effective, near-perfect broadband THz and IR absorbers based on CNTs films. In 2020, this group suggested and realized experimentally a design of graphene-VACNTs hybrids at THz region with simultaneously qualified operating bandwidth and sub-wavelength, as illustrated in Figure 10b.^[274] By appropriately designing the device structure to take advantage of the complementary THz absorption properties of CNTs and graphene, the device with an overall thickness of 260 μm has achieved an average absorbance of 0.98 over a wide band wavelength range of 0.2 to 3.0 THz and can operate stably in a wide range of incident angles up to 60° and in bending states. THz-to-IR conversion measurement confirmed that absorbed THz waves was converted into infrared thermal radiation, providing a promising and cost-effective opportunity for THz beam profiling, collimation, and focusing.

In order to achieve efficient absorption of light, the density of CNTs in VACNTs arrays is usually so low that they are fragile. In addition, VACNTs arrays can only be directly fabricated on rigid substrates such as silicon, and need to be transferred to desired flexible substrates through a subsequent transfer process, which further hinders the practical application of VACNTs arrays in large-scale flexible absorbers. In Figure 10c, Jin et al. have for the first time designed and manufactured a broadband omnidirectional perfect absorber based on trilayer super-aligned CNTs thin films suspended on a metal frame.^[275] Super-aligned CNTs networks can be prepared in a suspended manner, or directly on rigid and flexible surfaces, and show excellent mechanical robustness and surface durability. Thanks to the unique surface nanostructure of the super-aligned CNTs films and the inherent optical absorption properties of CNTs, the absorbers show excellent optical absorption performance. The average power absorbance of up to 99% is achieved in a wide wavelength range from UV (250 nm) to mid-IR (20 μm).

A promising approach to improve the omnidirectionality and polarization insensitivity of carbon-based nanostructured absorbers is to combine materials of various types, dimensions, and electrical/optical properties into three-dimensional hierarchical structures that provide synergistic effects in light harvesting.^[261] The random porous and oriented micro-nano structures in the hierarchical structures not only enhance the multiple internal reflections of incident light inside the device but also make the absorber insensitive to the angle and polarization of incident light. A variety of broadband perfect absorbers based on hierarchically porous carbon photonic structures, such as MWCNTs films on macroporous silica,^[276] and graphdiyne nanosheets on a copper oxide nanowire array,^[277] have recently been shown to have excellent light absorption properties and substantially enhanced incident angle independence, up to 50°. In 2020, Kiani et al. creatively developed a perfect ultra-broadband,

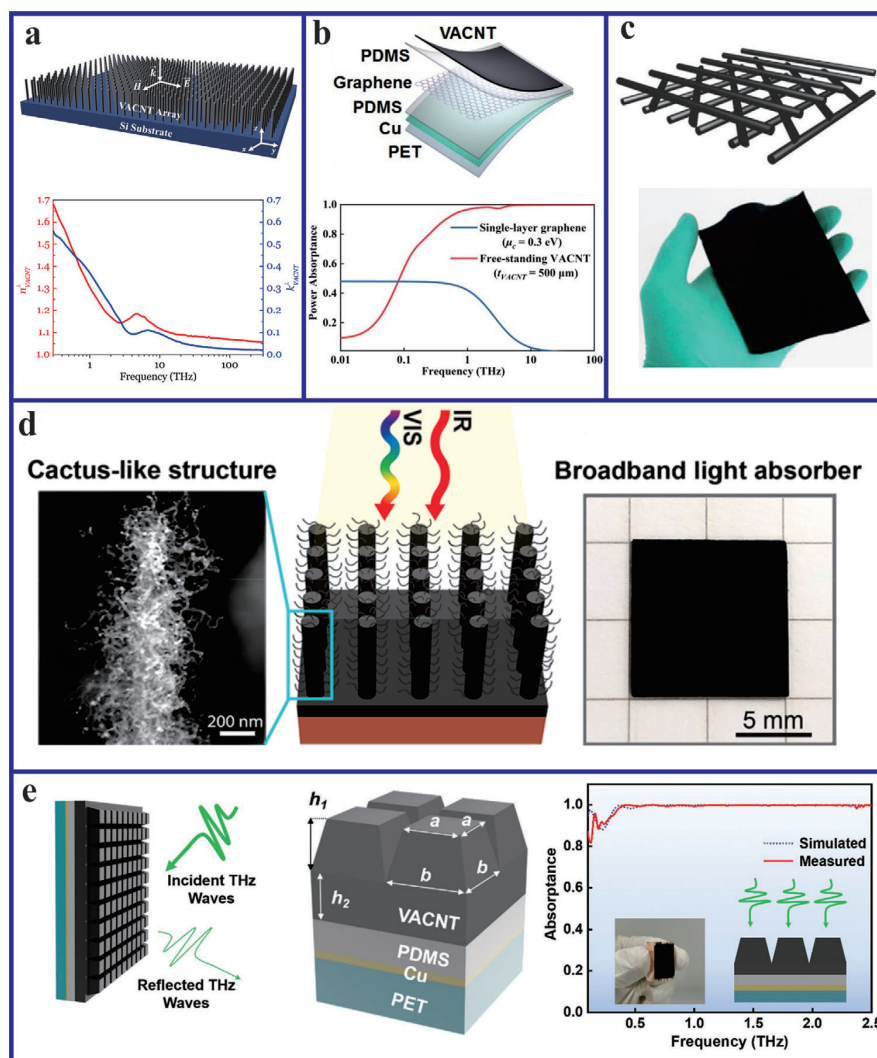


Figure 10. Various CNTs-based perfect absorbers in THz and IR bands. a) Top: Schematic illustration of a VACNTs forest for absorbing THz waves. Bottom: The effective complex refractive index of the VACNTs array as a function of frequency. Reproduced with permission.^[272] Copyright 2019, Elsevier Ltd. b) Top: A graphene-VACNTs hybrid THz perfect absorber. Bottom: Complementary power absorbances of free-standing VACNTs array and single-layer graphene. Reproduced with permission.^[274] Copyright 2020, Royal Society of Chemistry. c) Schematic illustration of a broadband omnidirectional perfect absorber based on trilayer super-aligned CNTs thin films. Reproduced with permission.^[275] Copyright 2020, Elsevier Ltd. d) Left: a field-emission SEM image of an individual cactus-like structure. Middle: Working principal diagram of synergistic light absorption of the hierarchical, cactus-like copper-CNTs nanowires structures. Right: A photographic image of the fabricated copper-CNTs nanowires structure. Reproduced with permission.^[261] Copyright 2020, American Chemical Society. e) Schematic diagram of a VACNTs array THz metamaterial absorber (Left) and the corresponding geometric dimensions of truncated pyramidal unit cells (Middle). Right: The measured and simulated power absorbance of the realized THz metamaterial absorbers within the 0.1 to 2.5 THz range. Reproduced with permission.^[280] Copyright 2022, John Wiley and Sons Ltd.

omnidirectional, and polarization-insensitive perfect absorber based on copper nanowire/CNTs cactus-like, hierarchical structure by combining the light-trapping properties of micro-scale copper nanowires with the excellent photoelectric properties of CNTs (Figure 10d).^[261] The copper nanowires and CNTs forest synergistically contribute to the as low as 0.75% average total specular reflection and 0.75% average total reflection, thus achieving near-unity light absorption within a wide range of in-

cidence angles up to 60° and a broad spectral range from VU to mid-IR. Due to the scalability of the fabrication process and extremely super light-absorption properties, this perfect absorber promises enormous potential for advancing a wide class of applications from energy harvesting to uncooled bolometric imaging and non-destructive testing.

Benefiting from the rapid development of femtosecond-laser microprocessing and transfer technique, CNTs-based THz

metamaterials and IR hyperbolic metamaterials devices are gradually proposed and experimentally implemented,^[37,47,278,279] which greatly enrich and enhance the performance of various CNTs-based optoelectronic devices in the THz and IR bands. More recently, the design, fabrication, and characterization of a THz metamaterial near-perfect absorber based on VACNTs arrays with truncated pyramid-shaped unit cells upon a polydimethylsiloxane /copper/ polyethylene terephthalate substrate have been demonstrated and experimentally verified, as shown in Figure 10e.^[280] The proposed fabrication technique can transfer the pyramid-shaped VACNTs arrays to the desired flexible substrate in a non-destructive way while maintaining the excellent surface morphology and optical absorption performance of VACNTs arrays. The experimental results show that in the wide frequency range of 0.1–2.5 THz, the THz metamaterials absorbers exhibit high uniform light absorption with an average power absorptance is more than 98%, which is in good agreement with the numerical simulation results. With different bending angles from 30° to 90°, no significant performance degradation was observed after 300 consecutive bending cycles, confirming the remarkable mechanical flexibility of the THz perfect absorber.

4.5. CNTs-Based THz Plasmonic Metamaterial Devices for Biochemical Sensing

Metamaterials usually refer to artificial electromagnetic materials with a variety of periodically arranged subwavelength unit cells that exhibit electromagnetic responses not found in natural materials, and have enormous potential for applications in miniaturization and integration of THz functional devices.^[281,282,124] The electromagnetic response of metamaterials can be flexibly tailored in any desired spectral range from microwave to UV simply by elaborately designing their unit cell structure.^[283–286] Noble metals, such as Au and Ag, are widely used as the medium to excite and propagate conventional SPPs, but metamaterial fabricated from these noble metals have been significantly hampered by the weaker confinement and increased losses at lower frequencies, and non-tunability once the geometry of the structure is fixed.^[287,288] Most importantly, the limited tunability of carrier density in metals is a primary obstacle to the development of actively tunable THz devices based on typical metallic metamaterials.

As a prototypical system of 1D structures, CNTs with their excellent electronic and optical properties make them a promising alternative candidate for THz to IR applications, the frequency range where their plasmonic resonance resides. Since the vibrational and rotational energy levels of biomacromolecules such as nucleic acids, proteins, and sugars fall in the THz range, one of the important applications of THz metamaterial devices is biochemical sensing at the THz frequency range.^[124,289] CNTs have a large aspect ratio and high electron mobility, which potentially improves sensor sensitivity and response time.^[124,290] Combined with their good biocompatibility and mechanical ductility, naturally render them an ideal platform for lightweight, low-cost, free-bending THz metamaterial sensors for environmental monitoring, and food and agricultural applications.

In 2021, Zhang et al. proposed a new composite THz metasurface which is composed of a CNTs resonant metasurface and a

silicon micro-fluid channel, as shown in Figure 11a.^[279] The absorption and refractive index sensing properties of the metasurface in the THz range were obtained by numerical simulation. The results show that the metasurface devices have obvious resonance absorption at 1.20 THz and 1.85 THz, with absorptance approaching 99.6% and 89.8%, respectively. In addition, this device has a good linear relationship between the position of the resonance absorption peak and the refractive index of the analyte in the microfluidic channel, and the frequency sensitivity can reach 492 GHz/RIU. In the same period, Zhou et al. proposed a CNTs-based THz metasurface consisting of two asymmetrically split rings that can generate bright-bright mode electromagnetically induced transparency, as shown in Figure 11b.^[291] The sensing properties of the metasurface device are further studied by covering the surface of the device with analytes of different refractive index. The change in the refractive index causes a significant change in the frequency position and amplitude of the resonance transmission peak. The calculated results show that the frequency sensitivity of the device for refractive index sensing is 320 GHz/RIU. Inspired by the remarkable flexibility of CNTs films, Zhang et al. demonstrated a flexible THz metamaterial based on CNTs film and studied its refractive index sensing properties.^[292] The simulation results show that when the refractive index of the dielectric layer changes from 1.33 to 1.58 at intervals of 0.05, a significant red shift occurs in the resonant frequency of the device. The resonance frequency position of the metamaterial changes from 0.947 THz to 0.906 THz as the refractive index of the analyte changes from 1.33 to 1.58.

The above research verified the feasibility of CNTs-based THz metasurface/metamaterial for biosensors from the perspective of theoretical analysis. In 2020, Wang et al. proposed and experimentally verified a novel ultrahigh-sensitivity THz metamaterial molecular sensor based on CNTs.^[293] As shown in Figure 11c, the sensor is composed of a SWCNTs cut line array on a silicon substrate. The experimental and simulation results show that the device exhibits strong reflection resonance at 0.4 THz when THz wave irradiates the metasurface, and its resonance frequency strongly varies with the composition of the substrate, the geometry of the periodic array, and the composition of the analyte. It is worth noting that when the device is used for molecular sensing of glucose, lactose, and chlorpyrifos-methyl, the minimum detection limits of the device are 30, 40, and 10 ng ml⁻¹ respectively. The ultrahigh sensitivity is attributed to the high tunability of CNTs and the effective adsorption of target analytes by CNTs through van der Waals force and $\pi - \pi$ stacking. This work not only innovatively proposes a THz metamaterial sensor based on CNTs films, but also provides a new insight for the study of ultrahigh-sensitivity molecular detection in the THz region.

In a parallel effort, Wang et al. developed and experimentally verified a THz metasurface sensor based on super-aligned MWCNTs arrays on the silicon substrate, as shown in Figure 11d.^[124] The normalized transmission spectra of the proposed device exhibit an obvious resonant transmission peak in the frequency range of 0.5–1.2 THz, which can be attributed to the surface plasmon polariton resonance on the device surface. When the sensor surface is loaded with different concentration gradients of pesticides (2,4-dichlorophenoxyacetic, 2,4-D), the sensor shows a good linear relationship between 2,4-D and transmission amplitude, and the critical value is 10 ppm. The results of a series of

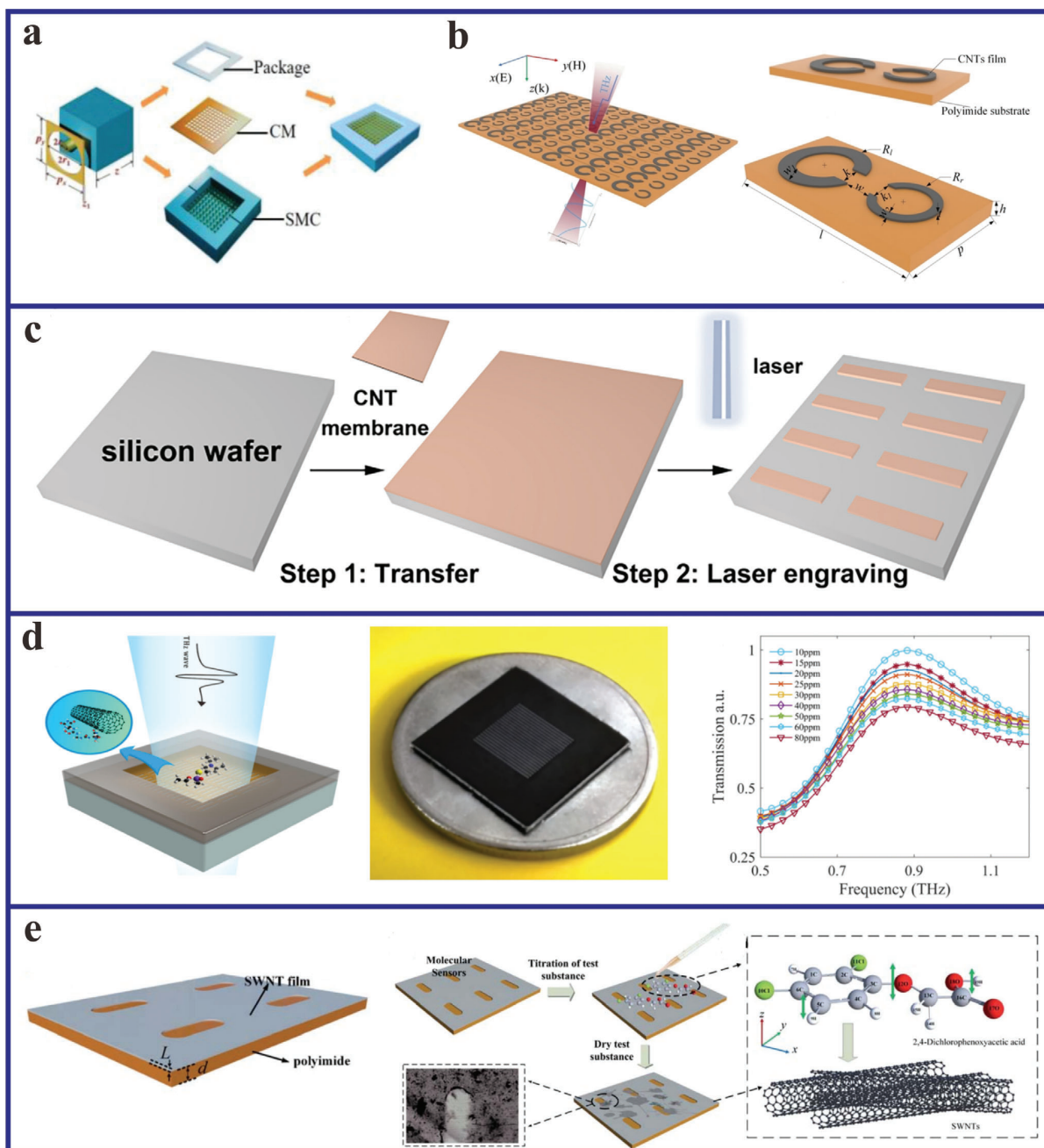


Figure 11. Various CNTs-based THz metasurface for biochemical sensing. a) A CNTs THz metasurface integrated with silicon microfluidic. Reproduced with permission.^[279] Copyright 2020, Frontiers Media S.A. b) Schematic structure of CNTs THz metasurface with two asymmetric split rings unit cell on polyimide substrate. Reproduced with permission.^[261] Copyright 2022, OSA Publishing. c) Schematic illustration of CNTs metamaterial fabricated by a two-step process. Reproduced with permission.^[293] Copyright 2020, American Chemical Society. d) Left: Schematic illustration of CNTs plasmonic metamaterial for pesticide detection. Middle: Optical image of the fabricated CNTs metasurface sensor. Right: THz transmission spectra of different concentrations of 2,4-d deposited by metasurface sensors. Reproduced with permission.^[124] Copyright 2020, American Chemical Society. e) Left: A SWCNTs-based THz metasurface with circular arcs unit cell. Right: Schematic diagram of pesticide detection process by a CNTs THz metasurface sensor. Reproduced with permission.^[132] Copyright 2022, Royal Society of Chemistry.

experiments show that the minimum sensitivity of the fabricated metasurface sensors has a value of approximately 2.0×10^{-3} /ppm, with the lowest detection mass of 10 ng and an error of 0.13% of reproducibility measurements. This work further verifies the feasibility of the application of CNTs-based THz metasurface devices in the field of sensing and detection and promises opportunities for the application of this device in THz detectors, wearable THz imagers, and other fields.

Most recently, Wang et al. developed and demonstrated a THz metasurface based on randomly oriented SWCNTs thin films that can be used for the detection of different concentrations of 2,4-D solutions, as shown in Figure 11e.^[132] The experimental results show that when the concentration of 2,4-D solution increases from 0 ppm to 8 ppm, the amplitude of the metasurface resonance transmission peak decreases from 1 to 0.79. There is a good linear relationship between the concentration of 2,4-D solution and the THz transmission amplitude. The metasurface sensor has a sensitivity as low as 2.1×10^{-2} /ppm and a minimum detection mass of 10 ng when it is used for 2,4-D detection at different concentrations by function fitting.

5. Conclusion and Perspectives

In conclusion, we have reviewed the groundbreaking early work and recent progress in CNTs-based THz functional devices. As presented in the review, over the past two decades, CNTs have yielded tremendously remarkable achievements and devices in the field of THz science and technology, especially among researchers who focus on electronic and optoelectronic applications. What is exciting is that CNTs exhibit truly unique photoelectric properties in the THz to the IR frequency band, whether individual nanotube at the nanoscale or CNTs films at the macroscopic scale. Additionally, these nanotubes are chemically, thermally, and mechanically stable, which promises them ideally suited for novel and efficient THz functional devices that are low cost, large area, flexible, compact, and operate at room temperature in the future THz technology. Currently, CNTs, as the pioneering and most widely exploited 1D nanocarbon material in THz frequency devices, the research focuses cover all forms of CNTs, including single CNTs, nanotube bundles or ropes, macroscopically random or aligned CNTs assemblies (films), and high-density horizontal or vertical CNTs arrays. At the same time, CNTs structures of interest have transferred from multi-wall to double-wall, then to single-wall, and material compositions from CNTs with mixed chirality to electronically pure semiconducting or metallic properties, and even to single chirality. CNTs-based THz frequency device architectures and concepts have evolved from onto-rigid substrates to flexible substrates, free-standing, and metasurface hybrid, demonstrating enormous technological advancement and broad application.

Although THz science and technology of CNTs have been extended to most fundamental and applied fields and substantial progress has been made, the application of CNTs-based THz devices still has plenty of challenges that lie ahead, among which the major obstacle is the efficient large-scale purification of CNTs. One of the most important ways to promote the performance of CNT-based THz functional devices is the employment of super aligned arrays of CNTs with single chirality, it is necessary to accurately control the preparation of CNTs, including the wall num-

ber, length, diameter, chirality, and degree of alignment. This is particularly essential for CNTs applications due to both the electronic and optical features of SWCNTs are extremely dependent on their structural parameters, orientation, and chirality. Though significant progress has been achieved in the preparation of defined-chirality SWCNTs via both direct-controlled chirality synthesis and post-treatment separation techniques, existing scalable production techniques only offer CNTs samples with an extensive range of chirality, and thus a method with low cost, high efficiency, high purity, and non-destructive that cannot introduce undesirable impurities into the growth and separation process is worth pursuing unrelentingly. More recently, Liu et al. demonstrated a multiple-dispersion sorting process that led to extremely high semiconducting purity (with a diameter distribution of 1.45 ± 0.23 nm and purity of >99.9999%) and a dimension-limited self-alignment procedure for preparing highly aligned CNTs arrays (within 9 degrees of alignment) with a tunable density between 100 to 200 CNTs per micrometer on a 4-inch silicon wafer with full wafer coverage.^[294] Furthermore, in 2022, Guo and co-workers creatively developed a non-destructive soft-lock drawing approach that allow the achievement of ultraclean SWCNTs arrays with a very high degree of alignment and a length/diameter ratio >200 000; these arrays can be aligned both straight or wavy, and are suitable for both metallic and semiconducting CNTs.^[295] These CNTs film arrays with both high density and high purity not only signify a breakthrough in developing CNTs for electronics applications, and but also may open a new approach toward the commercially viable fabrication of CNTs-based optoelectronic devices.

Improvements in CNTs preparation techniques combined with advances in theoretical research have led to a wider range of potential optoelectronic devices than are covered in this review. For instance, recent findings have revealed that packed, horizontally aligned films exhibit pristine in-plane hyperbolic properties in the mid-infrared range, where the effective dielectric constant is negative along the axis of nanotube alignment and positive in the vertical direction. This natural hyperbolicity on the surface is the desired platform to support highly confined hyperbolic polariton guided modes and has good prospects in many applications such as super-resolution imaging, super-resolution imaging, light propagation and manipulation, spontaneous emission engineering, biochemical sensing, and ultrafast light sources. In order to expand the range of THz imaging applications, stretchable, flexible optoelectronic systems have also attracted much attention recently. Kawano et al. pioneered this field in 2016 by developing a wideband (0.1-39 THz), flexible, and portable THz scanner based on an array of CNTs devices and performed THz imaging of three-dimensional curved objects.^[296] CNTs-based flexible and wearable THz systems are predicted to hold considerable application potential in non-destructive and non-contact detections, for example, medical examinations for the continuous monitoring of health conditions. Apart from the breakthroughs in the hybridization of CNTs and other carbon nanomaterials aforementioned in this review, photoelectronic devices, such as solar cells, photoresponsive transistors, and flexible and highly responsive photodetectors formed by the hybridization of CNTs and perovskite, are becoming another emerging research field that deserves attention. The performance of these hybrid optoelectronic devices is expected to be significantly

enhanced over devices made from CNTs or perovskite alone due to the combination of the excellent charge transport properties of CNTs and the superior light absorption of perovskite, which may enable CNTs-based THz frequency devices to enter the stage of commercial application as soon as possible. Moreover, periodic photonic systems, for example photonic crystals and metamaterial, present a diverse range of novel electromagnetic properties that are not found in materials in nature. CNTs can be exploited in integration with such extraordinary photonic platform to enable versatile device functionalities over a broad frequency band of the electromagnetic spectrum, such as bandwidth broadening, perfect absorption of light, polarization control, and so on.

Conventional semiconductor materials such as Si, GaAs, GaN, etc. are widely used in optoelectronic devices and modern integrated circuits due to their mature preparation technology and low cost. However, these traditional semiconductor materials usually can only absorb a specific frequency of light, which determines that its luminous wavelength range can only work in a specific band and the working efficiency is low, thus restricting the application of photoelectric devices in the THz and IR band. The quasi-one-dimensional nanostructures exhibit unique optical properties that are completely different from their thin film or bulk counterparts, namely excellent aspect ratio, high carrier mobility, and the ability to absorb ultra-wideband spectra. This unique and novel structure provides new opportunities for performance enhancement of optoelectronic devices in the THz and IR regime. Although nanotechnology is currently mature enough, its preparation cost is higher than that of traditional semiconductor materials, so it is expected that one-dimensional nanostructures such as CNTs can be integrated into traditional various THz functional devices in the future, thus solving the major challenges that have long hindered the commercialization of various THz applications including large size of the system, low efficiency, single operating frequency and diffraction limit spatial resolution. One example is the use of CNTs perfect absorption characteristics of light, CNTs as absorbers integrated into Si-based photodetectors, can achieve higher responsiveness and work efficiency. Furthermore, SWCNTs/semiconductor heterojunctions are known for their high photoelectric response, and can well solve the difficulties of charge separation and transport of photoexcited carriers of mixed chiral SWCNTs, and are therefore considered to have a good application prospect in the development of future optoelectronic devices. This new design strategy is expected to provide a feasible and simple way to improve the performance of THz and IR optoelectronic devices.

Although we anticipate some future trends and prospects in the field of CNTs based photoelectronic devices for THz and IR region, there is still a great amount of room for new research in this field. In fact, if progress had been made in the synthesis and characterization of nanomaterials, device engineering and manufacturing would proceed at the current pace, we undoubtedly believe that CNTs provide a feasible avenue to low-cost, tunable, and convenient THz devices for an extensive range of scientific, industrial, and potentially even consumer applications.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

Carbon nanotubes, optoelectronic devices, terahertz conductivity

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Yue Wang received the Ph.D. degree in microelectronics and solid-state electronics from Harbin Institute of Technology in 2011. From 2014 to 2015, He was a Research Scholar in College of Engineering, Boston University. He is currently a Professor with the Department of Applied Physics, and a High-level Talent at Xi'an University of Technology. He has been an Associate Director of the Key Laboratory of Ultrafast Photoelectric Technology and Terahertz Science. He was selected as one of World's top 2% of scientists in 2023. His research interest focuses on the THz spectroscopy of carbon-based nano-materials, surface plasmon polaritons, THz metamaterial and applications.



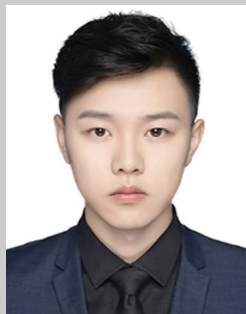
Guangcheng Sun received his B.S. degree in Physics from Xi'an University, China, followed by a M.S. degree in Physics from Xi'an University of Technology, China. Currently, He is working toward the Ph.D. degree in electronic science and technology at the Xi'an University of Technology, China. His research interests focus on carbon-based metamaterial and applications, natural hyperbolic properties of CNTs, and all dielectric THz metasurface and photonic crystal based on bound states in the continuum for applications in ultrasensitive biochemical sensing and nonlinear effects.



Xiaojun Zhang was born in Nanyang, Henan, China, in 1987. She graduated from Shaanxi Normal University with the master's degree in condensed matter physics in 2012 and is currently finishing the Ph.D. degree with the Xi'an University of Technology, Xi'an, China. Her current research interests include CNTs film, Si microfluidic channel, and the application of THz metamaterials.



Xiang Zhang was born in Yuling, China, in 1996. He received the B.S. degree in physics from the Baoji University of Arts and Sciences, Baoji, China, in 2019, and the M.S degree in physics from the Xi'an University of Technology, Xi'an, China, 2022. He is currently pursuing a PhD in electronic science and technology at Xi'an University of Technology in China. His research interest includes the all-dielectric THz metasurface and application as sensors.



Zijian Cui was born in Qiqihar, China, in 1995. He received the B.S. degree in electronic science and technology from the Harbin University of Science and Technology, Harbin, China, in 2017, and the M.S. degree in electric science and technology from the Harbin University of Science and Technology, Harbin, China, in 2020. He is currently pursuing a PhD in electronic science and technology at Xi'an University of Technology in China. His current research interests include THz metamaterials absorber, THz polarization converter, and phase gradient metasurface.