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Superaligned Carbon Nanotube Arrays, Films, and Yarns: A Road to Applications

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A superaligned carbon nanotube (CNT) array is a special kind of vertically aligned CNT array with the capability of being converted into continuous films and yarns. The as-produced CNT films are transparent and highly conductive, with aligned CNTs parallel to the direction of drawing. After passing through volatile solutions or being twisted, CNT films can be further condensed into shrunk yarns. These shrunk yarns possess high tensile strengths and Young's moduli, and are good conductors. Many applications of CNT films and shrunk yarns have been demonstrated, such as TEM grids, loudspeakers, touch screens, etc.

1. Introduction

Superaligned CNT arrays were first synthesized on silicon wafers using chemical vapor deposition (CVD) by our group in 2002; the resulting CNTs were well-aligned and formed into bundles by van der Waals forces. Continuous CNT yarns or films can be easily drawn from the superaligned CNT arrays. The process is similar to drawing silk from a cocoon. This "dry-drawing" approach provides a simple and natural way to obtain pure CNT yarns or films at a macro-scale and enables easy manipulation of nano-scale CNTs. Applications such as filaments for light bulbs and ultraviolet polarizers, utilizing yarns and films, respectively, were also demonstrated.[1] Since 2004, more groups have been attracted to this interesting field and have obtained continuous CNT yarns and films from CNT arrays using similar methods.[2–9]

There are three challenges for the applications of superaligned CNT arrays, films, and yarns: i) How to scale up the synthesis to meet industrial demand? ii) How to control the diameter and number of walls and eventually synthesize single-walled superaligned CNTs? iii) How to achieve real applications? Intense research efforts have focused on these issues. First, superaligned CNT arrays were successfully synthesized on four inch wafers in 2005,[10] and on eight inch wafers in 2008 (**Figure 1**a). Second, superaligned CNT arrays with diameter control were synthesized in 2007 and triple-walled superaligned CNT arrays were obtained.[11] Finally, many real

applications were demonstrated, such as field and thermionic emission electron sources,[12–14] high strength CNT yarns,[2,5,10,15–17] loudspeakers,[18] incandescent displays,[19] surface-enhanced Raman scattering (SERS) substrates,[20] electrodes for batteries and supercapacitors,[21,22] and CNT/polymer composites.[23,24] Real products of transmission electron microscopy (TEM) grids[25] and CNT touch screens [26] are ready to be commercialized. The discovery of continuous dry-drawn CNT films or yarns in 2002 opened a road leading to real applications of CNTs (Figure 1b).

2. Superaligned CNT Arrays, Films and Yarns

2.1. Superaligned Versus Ordinary CNT Arrays

A vertically aligned CNT array is a self-oriented nanostructure in which CNTs are vertically aligned and perpendicular to the substrate.[27] The merits of this ordered structure are high purity, high quality and quasi-unidirectional alignment. Metal catalyst contamination is limited except for the tips and roots of CNTs. The CNTs are quite straight as compared with curved CNTs derived from catalyst powders. The CNTs are aligned almost perpendicular to the substrate. Scanning electron microscopy (SEM) images of the ordinary vertically-aligned array show that the tubes are not perfectly aligned, but have some degree of randomness (**Figure 2**a). However, SEM images of superaligned CNT array show much better alignment than for ordinary ones (Figure 2a). Thus, the difference between superaligned and ordinary arrays is the degree of alignment – this is the reason the array is called "superaligned". Note that better alignment is the result of high nucleation density and narrow size distribution of catalysts. Thus, the first key feature of superaligned CNT arrays is the higher surface density and narrower CNT diameter distribution compared to ordinary arrays.

Strictly speaking, superaligned CNT arrays are distinguished from ordinary vertically aligned CNT arrays by the capability of being converted into continuous yarns or films in a dry state. It was proposed that the tangled top layer of the array is responsible for the capability of drawing yarns or films.[2,3] This is not the case, because they were found to be still drawable if the top layer was etched away by oxygen plasma.[26] Further evidence is that the superaligned CNT arrays become non-drawable if they are put into the furnace again and some amorphous carbon deposited on their surface. In this case, the tangled top layer

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a)

1cm × 1cm
(2002)

4inch Array
(2005)

8inch Array
(2008)

b)

Serendipity

Controlled Batch Growth

CNT Touch
Real Product
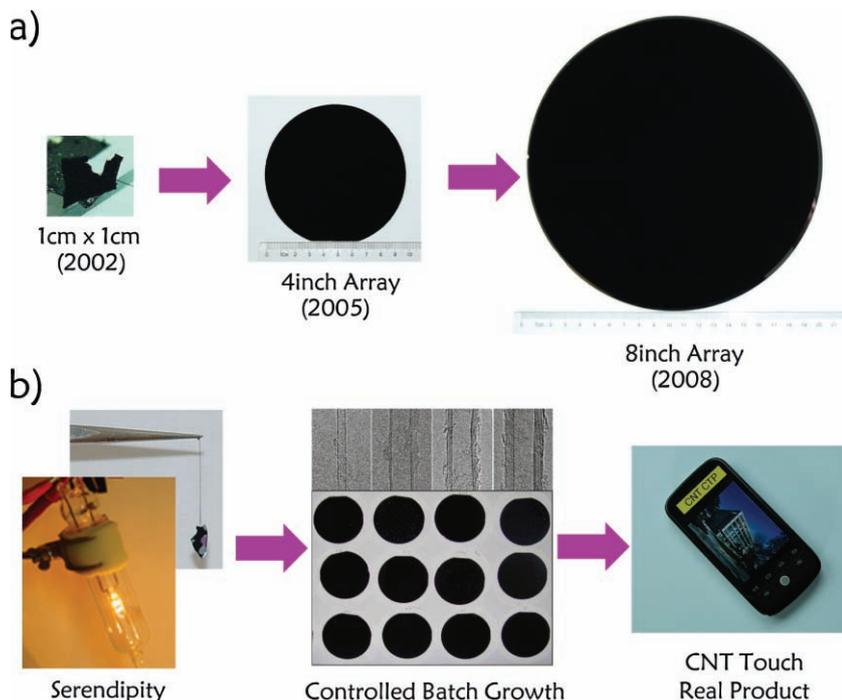
Figure 1. Superaligned CNT arrays: a) Controlled growth of superaligned CNT array with the size of 1 cm × 1 cm in 2002, Panels (a) and (b) reproduced with permission from [1], Copyright 2002, Nature Publishing Group, four inch in 2005, eight inch in 2008; b) The path, over the past eight years, from the basic discovery of superaligned CNT arrays to controllable batch growth, to physical properties and applications, and finally to real products.

used as precursor due to its low cost and low growth temperature.[1–3,7,10,11] Ethylene was also used as precursor to synthesize superaligned CNT with a relatively high temperature because ethylene needs to be thermally cracked before catalytic reaction with catalysts.[4–6] In both cases, one has to adjust growth parameters to guarantee high nucleation density and clean surfaces of CNTs. Following these basic principles, the growth of superaligned CNT arrays on silicon wafers was successfully scaled up with wafer diameters from 1 to 4 and then 8 inch (Figure 1a). To achieve batch growth, the challenge is maintaining the uniformity. A low-pressure chemical vapor deposition (LP-CVD) system was developed to achieve growth of superaligned CNT arrays with very good uniformity to meet the industrial requirements.

Despite these achievements, one fact remains: the synthesized superaligned CNTs are multi-walled CNTs (MWCNTs). For thin film transistor (TFT) applications, semiconducting single-walled CNTs (SWCNTs) are more desirable than MWCNTs. With superaligned SWCNT arrays, the fabrication process of TFTs will be much simpler: just pull out SWCNT films and stack on substrate for further mirco-processing. This will be a low cost and practical way of producing flexible TFTs, which will bring flexible displays into reality. Much effort has been devoted to this area. By controlling the size of the catalyst, the nanotube diameter and the number of walls can be successfully tuned from 15 to 6 nm and from ten-plus to three, respectively. The best result achieved so far has been the controlled synthesis of superaligned triple-walled CNT arrays.[11] There are still challenges in synthesizing superaligned SWCNT arrays. Work has also been done to obtain superaligned CNT arrays of various heights. The heights of the superaligned CNT arrays can be easily altered from less than 100 to 900 μm simply by tuning the growth time.[11] By using a high efficiency and long-life Fe catalyst film deposited on a thin Al_2O_3 buffer layer, drawable CNT arrays with heights up to 1.5 mm have been successfully synthesized.[4]

2.3. Superaligned CNT Films

2.3.1. Uniform CNT Films

The conversion process from superaligned CNT arrays to thin films is very simple. Just by using tweezers to pull out a CNT bundle, one can obtain a continuous ribbon the width of which is determined by the size of the initial bundles picked. If the superaligned array is of good quality, then an initial thin ribbon will be promptly extended to a CNT film with the same width as the substrate (Figure 2c). Alternatively by using a blade to scratch off a line of CNTs at the same time, one can directly obtain a CNT film of width equal to the length of the blade. For a good quality superaligned CNT array grown on an 8 inch

is still present, but the array become non-drawable. The amorphous carbon deposition weakens the van der Waals interaction and leads to a non-drawable array. The capability of drawing yarns or films actually originates from the strong van der Waals interactions between neighboring CNTs in the superaligned arrays. As is well known, clean surfaces lead to strong van der Waals interaction. Thus, the second key feature of superaligned arrays is the clean surfaces of CNTs.

To summarize, the prerequisites of being a superaligned rather than an ordinary array are narrow size distribution of catalysts, high nucleation density, and very clean surfaces of CNTs.

The narrow size distribution of catalysts and high nucleation density give rise to a large number of inter-tube contacting points, and the clean surfaces of CNTs result in strong van der Waals interactions. When you try to pull out a bundle from the superaligned array, the CNTs are end to end jointed by the van der Waals interaction, forming continuous yarns or films (Figure 2b).

2.2. Controlled Synthesis of Superaligned CNT Arrays

To synthesize superaligned CNT arrays, the basic principles are to achieve a narrow size distribution of catalysts, a very high nucleation density and to keep clean surfaces of CNTs. Usually, a high nucleation density requires a high level of supersaturation, which gives rise to high deposition rate of amorphous carbon on the surfaces of CNTs and so weakens the van der Waals interactions. Therefore, there is a trade-off in keeping high nucleation density and clean surfaces. Acetylene was

Figure 2. Superaligned CNT arrays, films, cross-stack films and shrunk yarns: a) SEM images of ordinary arrays and superaligned arrays; b) Schematic illustration of the proposed model for drawing yarns or films from superaligned CNT arrays; c) Optical image of drawing a transparent conducting film from eight inch superaligned CNT arrays; d) Schematic illustration of making superaligned cross-stack films and a TEM image; and, e) Schematic illustration of the process from superaligned CNT array to films and then to shrunk yarns.

per unit area is 1.5 μg cm^{-2}), transparent (78% at 550 nm for a single-layer film), conductive (typical sheet resistance is 700–1500 Ω per square for a single-layer film), and have ultra small heat capacity per unit area (7.7 × 10^{-3} J m^{-2} K^{-1} for a single-layer film).[18,26] CNTs are aligned in the drawing direction, which will result in polarization effect in both emitting and absorbing photons.[1,3,28]

2.3.2. Striped CNT Films

If the drawing direction is not parallel to the substrate but instead at a large angle, the obtained superaligned CNT films have a periodically striped configuration with alternating thinner and thicker film sections, and the width of the stripes is equal to the height of the original CNT arrays.[29] A video of the formation process of the striped film clearly shows the end-to-end joining process of CNTs, and thus validates the proposed model shown in Figure 2b. The CNT junctions are bottleneck positions for both thermal conduction and mechanical strength of the film, but not for electrical conduction. These films can be utilized as striped and high-degree-of-polarization light emission sources. These results are helpful for the basic understanding of the drawing process of superaligned films, and valuable for new applications and future large-scale production of tunable superaligned films of CNTs.

2.4. Superaligned CNT Cross-Stack Films

By cross-stacking several layers of superaligned CNT films, one can obtain a conductive and nanoporous network, which is termed a "cross-stack film" (Figure 2d).[20–25] The specific surface area of this cross-stack film has been measured to be 97 m^2 g^{-1} by the BET method.[22] The features of this cross-stack film include good conductivity, high mechanical strength and high specific surface area. The cross-stack films can be easily loaded with uniform nano-particles simply by physical deposition or thermal decomposition methods.[20–22]

2.5. Superaligned CNT Shrunk Yarns

If the superaligned films pass through some volatile solution, for example, alcohol or acetone, these CNT films will automatically be shrunk into tight fibers, with diameters depending on the width of the films.[10] For a film of 10 cm width, the diameter of the shrunk yarn is around 30 μm. The shrinking method gives rise to a yarn with tensile strength of 600 MPa, but the cross-section of the yarn is irregular.[10] Alternatively, the film can be twisted to a tight fiber.[2] The yarn made by the twisting method possesses a round cross-section but a tensile strength of 300–600 MPa.[2] A combination of the spinning and twisting methods gives rise to both a round cross-section and a much higher tensile strength of around 1 GPa (Figure 2e).[15] The tensile strengths of CNT yarns spun from ultra-long CNT arrays of 1 mm height can range from 1.35 to 3.3 GPa.[5,17] The features of the shrunk yarns include higher conductivity and much higher tensile strength than the films, the very light weight and much better flexibility compared to graphite fibers.

wafer, a pure CNT film of 20 cm width can be continuously drawn. The length of the film is dependent on the height of the array and the nucleation density. For an 8 inch CNT array with a height of 300 μm, a typical length of the film is 200 m. If the superaligned array is of bad quality, the width of the CNT films drawn out will be gradually decreased to zero, which means the CNT films cannot be obtained continuously but with a finite length.

The as drawn CNT films are quite thin, with typical thickness of tens of nanometers, depending on the height of superaligned CNT arrays from which it is drawn.[11] The ultrathin CNT films are therefore extremely lightweight (typical mass

3. Applications of Superaligned CNTs

3.1. Applications of Superaligned CNT Films

The as-drawn superaligned CNT films are composed of thin bundles of CNTs with unidirectional alignment, showing very appealing properties for optical devices, such as polarization effect, high transmittance of light and good conductivity. Many applications as optical devices have been demonstrated, which are described below. On the other hand, the superaligned films are extremely light in weight, and possess an ultra small heat capacity per unit area, which results in a very fast temperature response when current-heated. These unique thermal properties have led to applications such as incandescent displays, thermoacoustic loudspeaker, etc.

3.1.1. Polarized Light Source and Polarizer

Since CNTs are aligned in the drawing direction in the superaligned CNT films, this unidirectional feature will lead to some polarization effect in both light absorption and emission behavior.[1,3] Because the diameter of CNT is only around 10 nm, the movement of electrons is confined along the axial direction of the tube. If the polarization direction of incident photons is along the tube axis, the electrons will move with the E-field of the photon, and the energy of the photon is transferred to electrons and then dissipated into the lattice as heat. Thus, this photon is totally absorbed by the CNT. If the polarization direction of incident photons is perpendicular to the tube axis, the electrons cannot move with the E-field due to the confinement of the tube. The photons are thereby not absorbed and pass through the film. Therefore the as-drawn CNT film can be directly employed as an optical polarizer.[1] The advantage of CNT polarizer is that it can work at wavelength ranging from deep UV to far infrared.

On the other hand, when a current is applied through the film, electrons will be accelerated by the applied E-field and decelerated by lattice scattering. Again due to geometry confinement the movement of electrons can only be along the tube axis. The directions of acceleration and deceleration are both along the tube axis. According to the theory of electrodynamics, the photon emitted should be polarized along the tube axis,[30] and polarized planar light sources were constructed using superaligned films.[3,11,29]

3.1.2. Liquid Crystal Alignment Layers and Transparent Electrodes

An alignment layer is vital for the fabrication of high-quality liquid crystal displays (LCDs). The commercially available alignment layer for LCDs is a polyimide (PI) film that is mechanically rubbed to form some unidirectional grooves on the surface. Liquid crystal molecules are then inclined to align along the grooves. Since the superaligned films are composed of unidirectional CNTs aligned in the drawing direction, grooves with nanometer width will be naturally formed when the film is attached to the surface of a glass plate. It is then expected to possess the function of the alignment layer. At the same time, the CNT films are both conductive and transparent, which can also be utilized as the transparent electrodes for

LCD replacing costly indium tin oxide (ITO). The fabrication process is quite easy: first put the superaligned CNT film on the glass substrate, next deposit a very thin SiO_2 layer to fix the film and insulate the liquid crystal molecules from CNTs. The CNT film possesses both the function of the alignment layer and the electrodes (**Figure 3**a). Furthermore, it can be used as a built-in heating layer, which can extend the working temperature range of the LCDs. This superaligned CNT approach for LCD is a simple and easy to up-scale process and will lead to reduced cost of the fabrication process and facilities.[31,32]

3.1.3. Flexible Touch Screens

Touch screens have become indispensible in consumer electronics, because the most natural way of controlling something for human beings is to touch it with the fingers. Commercially available touch screens utilize indium tin oxide (ITO) transparent conducting films. ITO is a costly ceramic material and may crack under bending stresses. Superaligned CNT films are both transparent and conductive, and can replace the costly and brittle ITO to fabricate touch screens. Laser thinning and metal deposition methods were developed to improve the transmittance and conductivity of the superaligned CNT films to meet the industrial standard.[26] Real products of CNT touch screens are ready to be commercialized; these are 50 times better than ITO touch screens in scratch resistance and endurance tests. The superaligned CNT films enable the fabrication of flexible and curved touch screens (Figure 3b). Furthermore, the CNT touch screens integrated into mobile phones (Figure 1b) show superior performance in terms of endurance, flexibility and simple fabrication process.

3.1.4. Incandescent Display

The superaligned CNT films can be directly employed as a polarized incandescent light source. It has been found that CNT films in vacuum can be heated to incandescence and cooled down to room temprature in about 1 ms by switching on and off the applied current.[19] The high response speed is attributed to the ultra small heat capacity per unit area, large surface area and large radiation coefficient of the CNT films. A prototype 16×16 pixel CNT film incandescent display was fabricated using screen printing, laser cutting and pipe-free vacuum sealing technologies (Figure 3c). An individual pixel can reach a brightness of up to 6400 cd m^{-2} at 0.08 W. The CNT incandescence display can be driven by a simple addressing circuit and a dynamic incandescence display of Chinese characters was realized. The power consumption in the all-on state of 16×16 pixels is only 1 W. New devices based on a superaligned CNT film, such as addressable heaters, will also be easily developed.

3.1.5. Flexible Stretchable Transparent Loudspeakers

Once fed by audio frequency electric currents, superaligned CNT films can emit loud sounds. This phenomenon could be attributable to a thermoacoustic effect. The ultra small heat capacity per unit area of CNT films leads to a wide frequency response range (100 Hz to 100 kHz) and a high sound pressure level. Based on this finding, CNT thin film loudspeakers were
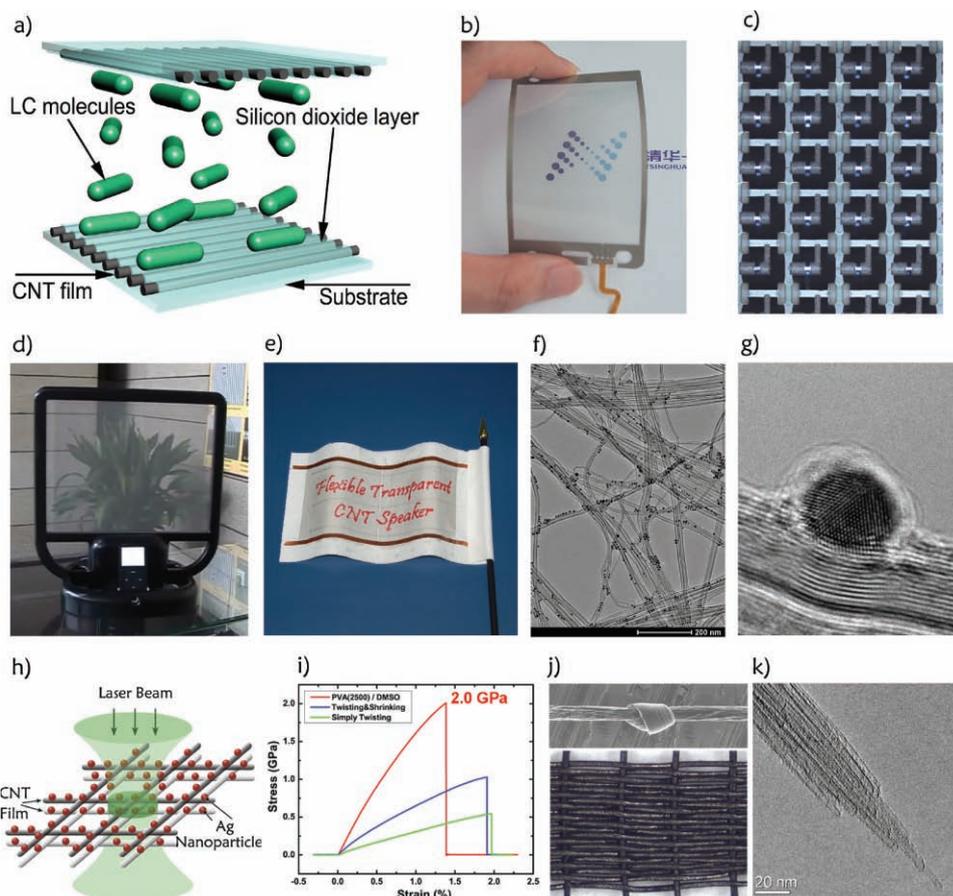
Figure 3. Applications of superaligned CNTs: a) Schematic illustration of the CNT alignment layer for LCD, reproduced with permission from [32], Copyright 2010, Elsevier; b) Optical image of the flexible CNT touch screen; c) Optical image of the incandescence display, captured under microscope; d) Transparent CNT loudspeaker; e) CNT loudspeaker put on a flag, reproduced with permission from [18], Copyright 2008, American Chemical Society; f) TEM image of gold nanoparticles supported by the CNT nano-grid; g) High-resolution TEM image of a gold nanoparticle supported by a CNT; h) Schematic illustration of the superaligned CNT SERS substrate. Reproduced with permission from [20], Copyright 2010, American Chemical Society; i) Stress–strain curve of the CNT/PVA composite yarn; j) The flexible CNT/PVA composite yarn can be woven into fabric, reproduced with permission from [16], Copyright 2010, American Chemical Society; and, k) Cone-like tip at the breaking point of a CNT yarn for field emission applications, reproduced with permission from [38], Copyright 2007, American Chemical Society.

fabricated, which possess the merits of being nanometer thick and transparent (Figure 3d), flexible, stretchable and magnet-free.[18] Such a single-element thin film loudspeaker can be tailored into any shape and size, freestanding or on any insulating surfaces (Figure 3e), which could open up new applications of and approaches to manufacturing loudspeakers and other acoustic devices. The applications of superaligned CNT films as thermoacoustic projectors can be further extended from air to underwater.[33] When the CNT sheet is immersed and wetted in liquid, the acoustic generation efficiency is severely degraded. However due to the high hydrophobicity of the CNT sheets in water, air cylinders outside the nanotubes can be formed to enhance the sound generation efficiency, which can exceed those of much thicker ferroelectric acoustic projectors at frequencies below 4 kHz.

3.1.6. Giant-Stroke and Superelastic Muscles

Superaligned CNT films can be used as new artificial muscles that are driven by an applied voltage and can provide giant

elongations of 220% and elongation rates of (3.7×10^{4})% per second at operating temperatures from 80 to 1900 K.[34] The density of the CNT films are as low as approximately 1.5 mg cm^{-3} and their specific strength along the axial direction is higher than that of steel. CNT films with decreased density by actuation can be permanently frozen for use as transparent electrodes. The Poisson's ratio of the CNT film reaches 15, which is 30 times higher than those of conventional rubbers. These giant Poisson's ratios result in rare properties of the CNT films, such as negative linear compressibility and stretch densification.

3.2. Applications of Superaligned Cross-Stack CNT Films

The cross-stack CNT films possess a nanoporous structure, good electrical conductivity, high mechanical strength and huge specific surface area. These excellent properties make it an ideal TEM grid for nano-scale characterization.[25] The CNT nano-grids can be further deposited with gold or silver nanoparticles,

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possessing additional functions as a SERS substrate,[20] or can be loaded with oxide nanoparticles to work as electrodes for lithium ion batteries and supercapacitors.[21,22] The cross-stack CNT films can also be integrated into a polymer matrix to dramatically improve the mechanical and electrical properties of CNT/polymer composites.[23,24]

3.2.1. Superaligned TEM Nanogrids

Characterizations of nanomaterials by high resolution transmission electron microscopy (HRTEM) are becoming indispensable today, especially for those working in the field of nano-science and nanotechnology. Conventional TEM microgrids are fabricated by depositing an ultrathin layer of amorphous carbon on a copper mesh. However for nanoparticles having diameter less than 5 nm, it is difficult to obtain clear HRTEM images due to the interference from the amorphous carbon. To overcome this difficulty, a cross-stack CNT film was stacked on a copper mesh to make a CNT nanogrid for TEM observation. The merits of this CNT nanogrid include a novel nano-holey structure with a large number of nanosized holes and numerous effective edges, good conductivity, high mechanical strength and strong adsorbability inherited from the carbon nanotubes. Clear HRTEM images of different nanoparticles and nanotubes were obtained (Figure 3f and g). CNT nanogrids show performance superior to conventional microgrids for characterization of ultrafine nanostructures (Figure 3g). The lattice distance between adjacent graphene layers in carbon nanotubes can serve as a natural scale bar (Figure 3g). Furthermore, the batch fabrication process of the CNT nanogrids is fully automatic with very high production rates.[25] The CNT nano-grids are ready to be commercialized.

3.2.2. Superaligned SERS Substrate

SERS has attracted wide interest due to its capability of enhancing normally weak Raman signal by several orders of magnitude and facilitating sensitive detection of molecules. Conventional SERS substrates are fabricated by depositing metal nanoparticles on a planar substrate. The planar substrate can be replaced by the cross-stack CNT film and the enhancement effect can be dramatically improved. This highly sensitive nanoporous SERS substrate can be easily fabricated in batches and at low cost by physical evaporating Ag nanoparticles on the cross-stack CNT films, resulting in unique zero-dimensional Ag nanoparticles on one-dimensional CNT nanostructures (Figure 3h). The as-prepared transparent and freestanding CNT SERS substrate is capable of detecting ambient trinitrotoluene vapor, showing much higher Raman enhancement than ordinary planar substrates because of the extremely large surface area and the unique structure combining zero-dimensional nanoparticles with one-dimensional CNT nanostructure. These results not only provide a new approach to ultrasensitive SERS substrates, but also are helpful for improving the fundamental understanding of SERS phenomena.[20]

3.2.3. Electrodes for Lithium Ion Batteries and Supercapacitors

Energy storage device plays a vital role in daily life. Much effort has been devoted to improve their energy density and lifetime. Some oxides can greatly improve the energy density, for example, SnO_2 can improve the energy density of lithium ion battery, and Mn_2O_3 can improve the capacity of supercapacitors. For both kinds of energy storage devices, the typical structures of the electrodes are a metal foil current collector covered by a layer of oxides. Frequently encountered problems include the bad conductivity of oxides that limits the rate performance, and the capacity fading due to the aggregation and volume change of oxides. To solve these problems, electrodes were fabricated by loading oxide nanoparticles on the cross-stack CNT films. The cross-stack CNT films serve as both dispersed current collector and support of oxides nanoparticles, which facilitate the electron transfers from oxides to CNTs directly. On the other hand, the nanoporous structure can greatly avoid aggregation and accommodate the volume change of oxide nanoparticles. The fabricated lithium ion battery and supercapacitor show excellent performance in terms of capacity, rate and cycle performance. The constructed SnO_2@CNT lithium ion battery can deliver over 850 mA h g^{-1} of charge capacity with 100% retention for at least 65 cycles when cycled in the potential window 0.01–3 V versus Li$^+$/Li.[21] The Mn_2O_3@CNT supercapacitor shows high specific capacitance (around 500 F g^{-1}, including the current collector mass), reliable electrochemical stability (<4.5% degradation in 2500 cycles) and a very high rate capability (245 F g^{-1} at 155 A g^{-1}).[22]

3.2.4. Composite Materials Applications

As one of the most promising composite materials, CNT/polymer composites need to be fabricated on a large scale and have excellent properties, including mechanical and physical properties, for practical applications. CNT films were stacked together to form preforms with thickness on a centimeter scale. Thus, it is possible to macroscopically fabricate CNT/polymer composites using methods that are suitable for making carbon fiber-reinforced composites, such as resin transfer molding (RTM) by infiltrating liquid resin into the CNT preform and curing the resin. CNT/polymer composites with homogenous dispersion, high loading and controllable orientation of CNTs were successfully fabricated. Both mechanical and electrical properties of the CNT/polymer composites were dramatically improved. Composites with specific properties along various directions can be designed by controlling the volume fractions and orientation of the CNT films. Such composites can be made on a large scale and used as multifunctional materials for practical applications such as electrostatic dissipation (ESD) and electromagnetic interference (EMI) shielding.[23,24]

3.3. Applications of Superaligned CNT Yarns

Superaligned CNT yarns possess good electrical conductivity, high mechanical strength and the capability of emitting electrons either at high temperature or under an electric field. Applications of CNT yarns as high strength conductive fibers[10,15,16] and thermionic and field emission electron sources[12–14] have been explored.

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3.3.1. High Strength and Conductive Fibers

High performance (high strength and high modulus) fibers, such as Kevlar and graphite fiber, etc., are of great importance in industrial, military and aerospace applications. Individual CNTs are more than 20 times stronger than Kevlar and graphite fibers and, thus, have great potential in the field of high performance fibers. As shown above, CNT films can be twisted or shrunk into tight fibers. A combination of twisting and shrinking gives rise to CNT yarns with tensile strength of 1 GPa.[12] Even though the tensile strength is not as high as the aforementioned high performance fibers, it is a good conductor and extremely flexible. To further improve the strength of CNT yarns, composite fibers were made by embedding CNTs in a polymer matrix. However, the conductivity was severely decreased.[2] To enhance both the strength and conductivity, CNT films were first twisted into round fibers, then passed through a PVA/dimethyl sulphoxide solution, and finally dried by passing through a furnace. The as-produced CNT/PVA composite yarns possessed very high tensile strengths of up to 2.0 GPa (Figure 3i), Young's moduli of more than 120 GPa, and electric conductivities as high as 9.2×10^4 S m^{-1}. These composite yarns are flexible, lightweight, scratch-resistant, very stable in ambient and resistant to extremely humid environment. They can be further woven into high-strength and heatable fabrics (Figure 3j), showing great potentials in applications such as flexible heaters, bulletproof vests, radiation protection suits and spacesuits.[16]

3.3.2. Thermionic and Field-Emission Electron Sources

CNT yarns have a moderate work function of around 4.5 eV, which is a little bit smaller than that of tungsten. Due to its high strength, good flexibility, and stability, CNT yarn can replace tungsten wire to serve as a thermionic emission electron source that can stably work at 2 000 K.[28,35] To further increase the lifetime of the CNT thermionic emitter, one has to lower the working temperature. A practical way is to modify the CNT yarn with some low-work-function materials. Barium-functionalized CNT yarns were fabricated by drawing and twisting the CNT yarns through a solution containing barium nitrate. After heat activation under vacuum, the functionalized yarns were enriched in barium oxide due to the high surface-to-volume ratio of the nanotubes. The cathodes exhibited good thermionic properties, with a work function as low as 1.73–2.06 eV and thermionic current density over 185 mA cm^{-2} at 1 317 K. The barium-functionalized yarns have high tensile strength of up to 420 MPa and retain strength of 250 MPa after a 2 h period of activation.[36]

Due to the nanometer-size tips and high aspect ratio of CNTs, the field enhancement factors should be huge, which make CNTs ideal field emission electron sources. Simply breaking the shrunk yarns into pieces, each piece of CNT yarn can serve as a field emitter. The emission current can reach several milliamperes (for yarns with diameter of 30 μm), and the emitters can work stably for a long time. The excellent field emission properties are due to the large enhancement factor, over 100 000, dense emitting centers and the robust structure. The emitters can be manipulated and assembled into devices, such as electron guns, x-ray tubes and pixel tubes, etc.[37] The advantage is the high emission current and the disadvantage is the poor coherence of emitted electrons. For applications such as field emitters for TEM, the coherence of electrons is very important for the quality of TEM images. To meet this requirement, a laser irradiation assisted vacuum breakdown method was developed to fabricate taper shaped yarn, of which the tip is an individual CNT. This unique structure possesses excellent mechanical stability, good thermal and electrical conductivities, and most importantly the high degree of coherence of the emitted electrons due to the extremely small emitting area.[38]

For a field emission vacuum gauge that might work at rough vacuum, the field emitter should be very stable under ion bombardment. To meet this requirement, HfC-decorated CNT yarn emitters were fabricated by pre-coating pure CNT yarns with Hf and then current heating to 1600 K in vacuum to form HfC nanocrystals through reaction of the CNTs with Hf. The fabricated HfC–CNT yarns have a work function of 3.9 eV, lower than that of pure CNT yarns. Following the same vacuum breakdown process, HfC–CNT sharp tips were obtained with an emission current of 320 μA. The emitters could operate under a rough vacuum of 10^{-2} Pa without obvious degradation.[13]

4. Conclusions

Tremendous achievements have been made in nanoscience and nanotechnology, from the basic discovery of superaligned CNT arrays, to controllable batch growth, then modification of physical properties and applications, and, finally, real products. Many real applications, such as field and thermionic emission electron sources, high strength CNT yarns, electrodes for batteries and supercapacitors, loudspeakers, incandescence displays and SERS substrates, have been demonstrated. Real products of TEM grids and touch screens are ready to be commercialized. More and more superaligned CNT products will come to the market in the near future.

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