Spinnable Carbon Nanotubes for Advanced Technological Applications

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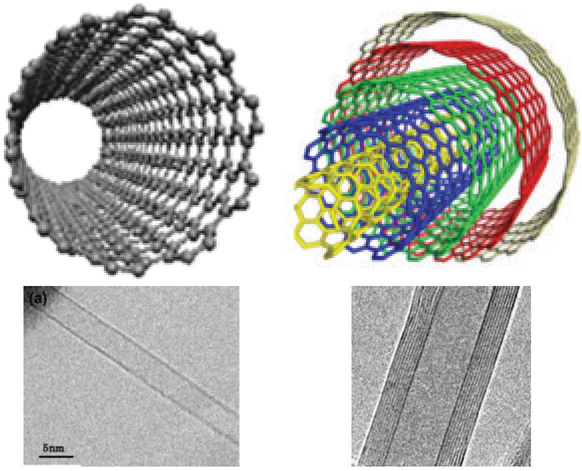
Introduction

Carbon nanotubes (CNTs) have become a focal point of extensive research since its discovery by Ijima in 1991 [1]. Over the past few decades, their remarkable properties, including high mechanical strength, robust electrical characteristics, efficient heat conductance, and notable electron emission, have captured the attention of both academic researchers and industries [2]. Carbon nanotubes exhibit diverse potential applications, serving as electrodes for electrochemical double-layer capacitors, field emitters, components in biomedical applications, materials for fibers and fabrics, contributors to nano-electronic devices, agents for EMI shielding, building blocks for hydrogen storage nano-tanks, and functional polymers, among other uses [3].

CNTs can be broadly classified into two categories based on their structural configuration: Single-walled carbon nanotubes (SWCNTs) and Multi-walled carbon nanotubes (MWCNTs). SWCNTs consist of a single-wall graphene rolled into a cylindrical tube, while MWCNTs are composed of multiple layers of graphene rolled into cylindrical tubes, as depicted in Figure 1. Figure 1 shows the schematic diagram of SWCNT and MWCNT together with their Transmission Electron Microscope images (TEM).



(a) (b)

Figure 1. Schematic structure and TEM image of (a) SWCNT (b) MWCNT

Furthermore, CNTs can be classified into three groups based on their chirality: Armchair, Zigzag, and Chiral nanotubes. Armchair nanotubes, with chiral indices (n,n), exhibit metallic properties. In contrast, Zigzag nanotubes, characterized by chiral indices (n,0), display either metallic or semiconducting properties depending on the value of (n). Chiral nanotubes, having general chiral indices (n,m), demonstrate a range of electronic properties, encompassing both metallic and semiconductor behavior [4]. The chirality of SWCNTs defines their structural and electronic characteristics. Due to the multiple walls in MWCNTs, they inherently exhibit a variety of chiralities within the same structure, resulting in consistent metallic properties.

The synthesis of Carbon nanotubes (CNTs) can be achieved through various methods, each with its own set of advantages and limitations. Common techniques include Arc discharge, Chemical vapor deposition (CVD), Laser ablation, and Template-assisted synthesis. Among these methods, Chemical vapor deposition (CVD) stands out as the most effective for large-scale control of CNTs in recent years due to its simplicity, ease of operation, and lower cost [5].

Individual CNTs possess an electrical resistivity ranging from 10^{-4} to 10^{-5} Ω cm [6], a tensile strength of 150 GPa [7], and a thermal conductivity of 3500 W/m K [8]. Despite their vast application potential, utilizing pristine CNTs on a macroscopic scale is challenging, except in randomly oriented composites. To fully unlock their potential at the macroscale, it is imperative to organize them into highly ordered structures such as aligned webs or yarns. A sophisticated approach to achieving this involves synthesizing CNT forests that can be directly spun from the growing substrate into highly aligned webs or yarns.

Figure 2 illustrates non-aligned spaghetti-typed CNTs synthesized through the CVD method. These CNTs find applications where they are oriented in random directions to achieve optimal properties.

Additionally, utilizing pristine CNTs in macroscopic applications may not yield the best properties, as these CNTs are directed in random orientations.

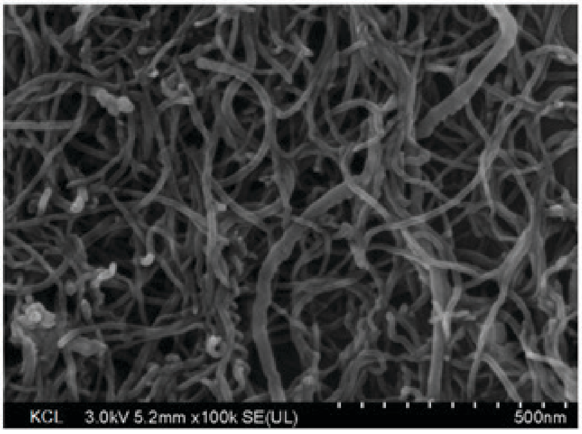


Figure 2. SEM image of spaghetti-typed CNTs

Figure 3 depicts the SEM image of a CNT forest, which is not spinnable, grown by the CVD method. Despite these CNTs are aligned in single direction, utilizing these CNTs in macroscopic applications in pristine configurations, remains challenging due to handling difficulties. Consequently, when incorporated into applications, they are often oriented in random directions.

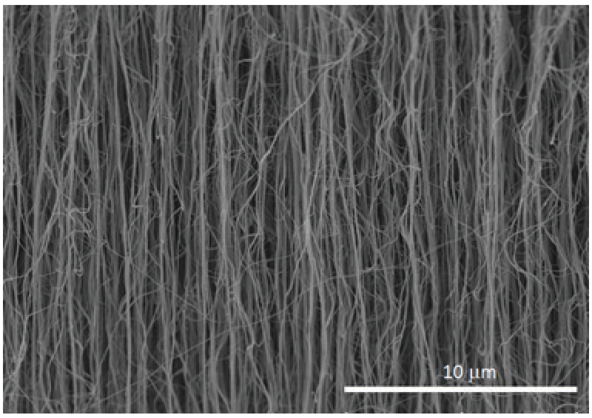


Figure 3. Aligned-CNT forest grown by the CVD method

Spinnable Carbon Nanotubes

Spinnable CNT forest are super vertically aligned CNT array that can be spun directly into yarns or webs. These specialized CNT forests can be synthesized using a controllable CVD method [9]. The resulting spinnable CNTs find valuable use in macroscopic applications in the pristine configurations, functioning as thin films, webs, or yarns. Their single-direction alignment in the sheet and yarns allows for the maximum exploitation of their properties in specific applications.

Figure 4 presents both the optical image and SEM image of spinnable CNT forests synthesized through CVD. The grown CNTs exhibit a high degree of alignment in a single direction, making it feasible to spin them into yarn or sheet. CNT sheet and yarn production method are illustrated in figure 5 and figure 6 respectively. The ease of use and the ability to harvest the maximum properties of these CNT yarns and sheets make them suitable for various applications.

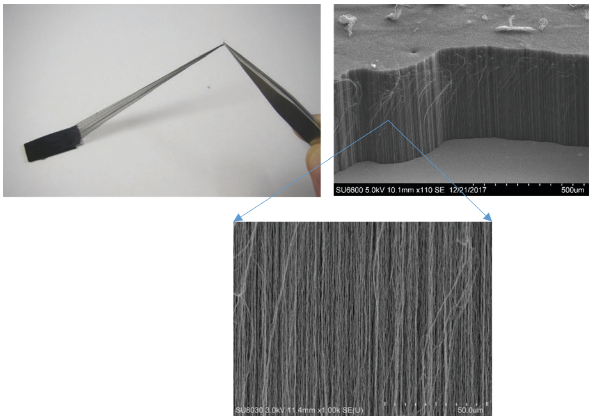


Figure 4. Optical image and SEM image of spinnable CNT forests

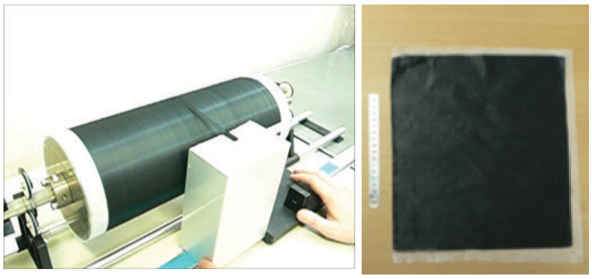


Figure 5. CNT sheet production by super aligned CNT array

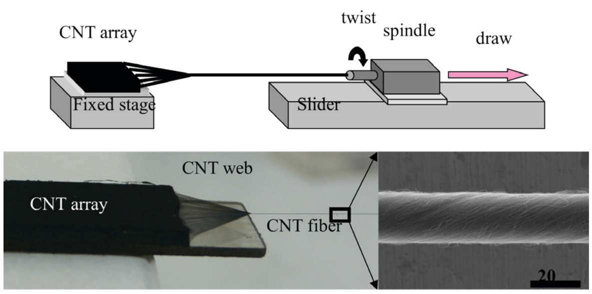


Figure 6. CNT yarn production by super aligned CNT array

Growth of Spinnable CNTs

Spinnable CNT array is grown using the CVD method which enables the controlled growth of carbon nanotubes on a substrate, typically a metal catalyst layer applied on the substrate and specific reaction conditions, including pressure and temperature. Spinnable CNT forest shown in the figure 4 illustrates CNT forests grown on a quartz substrate via the CVD method, employing a catalyst of $FeCl_2$, a chamber temperature of 800 °C, and a pressure of 3 torr. Researchers practice different CVD chamber condition and catalyst materials to synthesis spinnable CNT forest on substrate. Inoue et al. have used $FeCl_2$ catalyst and acetylene gas for synthesizing spinnable CNT forest with CVD chamber temperature of 800 °C, and a pressure of 3 torr [9]. Hawking et al. have used iron catalyst, helium and acetylene gas for synthesizing spinnable CNT forest with CVD chamber temperature of 670 °C [10].

Requirements for Spinnability

To ensure continuous spinnability from the grown CNT forest, several key requirements must be satisfied:

1. High areal density of CNTs (> 109 CNTs/cm^2)
2. Super vertical alignments
3. Crystalline structure with few defects and high purity

Though vertically aligned CNTs were successfully grown on the substrate, continuous spinnability or drawability cannot be achieved without proper areal density of CNTs on the substrate. It has been observed that number of vertically aligned CNTs exceeding 10^9 exhibit continuous spinnability, as demonstrated in Figures 5 and 6. Moreover, super vertical alignment is equally crucial for continuous spinnability, as evidenced in Figure 4. For example, even with sufficient areal density, undulated CNT arrays, as shown in Figure 7, lack spinnability due to a lack of super vertical alignment.

Moreover, the crystallinity of the grown CNTs plays a vital role in continuous spinnability and drawability. CNTs remain connected while being drawn or spun by Van der Waals forces. Defects on individual CNTs weaken the Van der Waals interaction among CNTs, thereby compromising spinnability. Figure 8 illustrates the connectivity of CNTs through Van der Waals forces during the drawing or spinning process from CNT super-aligned arrays. The crystallinity of CNTs can be measured using Raman spectroscopy analysis. Figure 9 shows the Raman spectroscopic analysis of spinnable CNT array where the graphene peak (G band) is higher than the defects peak (D band). Another important factor for spinnability is purity. Purity is crucial for enhanced Van der Waals interaction between individual CNTs, requiring minimal adherence of catalyst particles and amorphous carbon deposition.

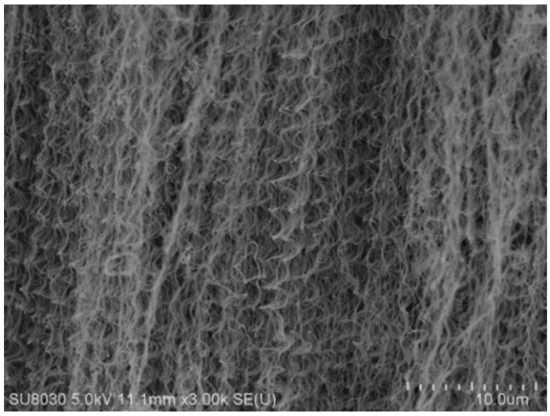


Figure 7. SEM image of vertically aligned undulated CNT forest

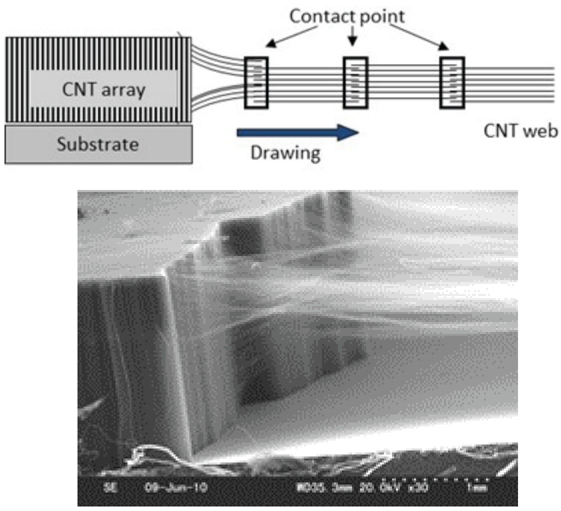


Figure 8. (a) Schematic diagram of drawing mechanism of spinnable CNTs and (b) SEM image at drawing the CNT web.

Application of Spinnable CNTs

Non-spinnable general CNT powders find utility in various applications such as composite materials, batteries, supercapacitors, EMI shielding, biomedical applications, sensors, catalysts, water purification, electronic devices, and gas storage etc. However, several of these applications can be enhanced by replacing traditional CNT powders with spinnable CNTs, inducing their superior structural properties and straightness.

The unique significance of spinnable CNTs lies in their capacity to form CNT yarns and sheets. These can be employed in diverse applications, including replacing conducting wires, energy storage (batteries and supercapacitors), high-strength cables, textiles, lightweight structural components for spacecraft, reinforcement in composites, flexible electronics (wearable electronics, smart fabrics, and flexible displays), conductive films and coatings (touchscreens, solar cells, and antistatic materials), and strain sensors integrated into structural materials, among other uses.

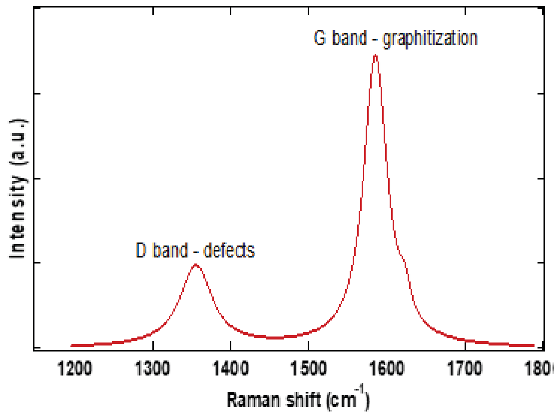


Figure 9. Raman spectroscopy of spinnable CNT array

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