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Fluffy carbon nanotubes produced by shearing vertically aligned carbon nanotube arrays

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ABSTRACT

Fluffy carbon nanotubes (CNTs), which are cotton-like macroscopic structures, are obtained by simple high-speed shearing of vertically aligned CNT (VACNT) arrays. The fluffy CNTs are composed of CNT bundles with a diameter of several micrometers, and have an extremely low apparent density of 3–10 g/L. A requisite for their formation is the alignment of CNTs in the initial array. The shear between the rotor and the arrays tears the arrays along the axial direction and this results in their dispersion into low density fluffy CNTs.

High performing macroscopic carbon nanotubes (CNTs) have attracted significant attention recently. According to the research, applications for these macroscopic structures include CNT arrays, CNT yarns, CNT papers, CNT films, CNT sheets, CNT membranes, and CNT fibers. High performance in various aspects, such as strength, elasticity, and conductivity depend largely on the aspect ratio and the arrangement of CNTs. It has been noticed that vertically aligned CNT (VACNT) arrays have become the basis for transformation into certain CNT macroscopic structures [1]. To date, VACNT arrays have been mass produced by radial growth on ceramic spheres [2], after which they can be used in composite applications. The dispersion of CNTs is the first step in constructing composites. Various methods, including sonication [3], milling [4–8], acid treatment, and functionalization [9], have been extensively used for CNT dispersion in solutions. The surfac-

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tants [3,9], polymers, or biomolecules grafted on CNTs, improve CNT dispersion in certain solutions. However, it was found that the CNTs were contaminated during those processes. Milling has a significant advantage for large-scale treatment [4–8]. However, most researchers use agglomerated CNTs for ball milling or shearing in the liquid phase, introducing addition difficulty in separation for further application [4–8]. Since CNTs always grow in the gas phase, if methods for CNT dispersion in the gas phase are developed, the complications for CNT dispersion in the solution route, such as CNT agglomerates formation and solvent separation would be avoided.

In this study, a simple high-speed shearing method was developed to disperse a VACNT array in gas phase. Fluffy CNTs with a cotton-like macroscopic structure were obtained directly after high-speed shearing. Fluffy CNTs were composed of CNT bundles of several micrometers in diameter. In each fluffy CNT bundle, the CNTs were still in good alignment. In addition, they exhibited an extremely low apparent density and high porosity. Hence, the fluffy CNTs can serve as a good basis for further macroscopic CNT construction.

Previous studies about the synthesis of long VACNT arrays have been undertaken [10], and the detailed shearing process has been video-recorded. The process involved placing a 0.5 g VACNT array into a high-speed stamping shearer. The thickness of the rotor was 0.5 mm. After shearing for 15~60 s, fluffy CNTs were obtained. Photos of the VACNT arrays and fluffy CNTs were taken using a Ricoh R4 video camera. The morphologies were further characterized using a JSM 7401F scanning electron microscopy (SEM). Using statistics from the SEM images, the diameter distribution of CNT bundles was obtained.

VACNT arrays were synchronously grown and perpendicular to the quartz substrate using the floating catalyst method. After eight hours of growth, the length of CNT array reached 8 mm (Fig. 1a). Fig. 1a reveals that the CNTs were in array form even when they were peeled off from the substrate. The density of VACNT array was approximately 20 g/L, which could be further modulated by adjusting the growth conditions. In this study, the length of the VACNT arrays was 6~8 mm. As shown in the video (see Supplementary material), the VACNT arrays were placed in a high-speed shearer with a rotor capable of rotating at a speed of 24,000 r/min. Compared with high shearing speed of motor rotor, the VACNT array was rotated at a relatively low speed. When meeting the rotor, the VACNT arrays were torn into large pieces by strong shear force between the rotor and the arrays. After shearing for 15 s, the VACNT arrays became fluffy and the volume of the fluffy CNT increased noticeably (Figs. S1–S9). With continued shearing, the VACNT arrays were torn into smaller pieces and the volume further increased. Thus, fluffy CNTs composed of small CNT bundles were obtained, as shown in Fig. 1b. Direct application of force on a single CNT in a short shearing time proved to be difficult. Thus, the CNT length remained long.

The microscopic morphology of the fluffy CNTs is shown in Fig. 2a and Fig. S10. The fluffy CNTs were bundles with a length of 6 ~ 8 mm and a diameter of 5 ~ 50 μm. The relationship between shearing time and the apparent density and the bundle diameter are presented in Fig. 2b. At the beginning,

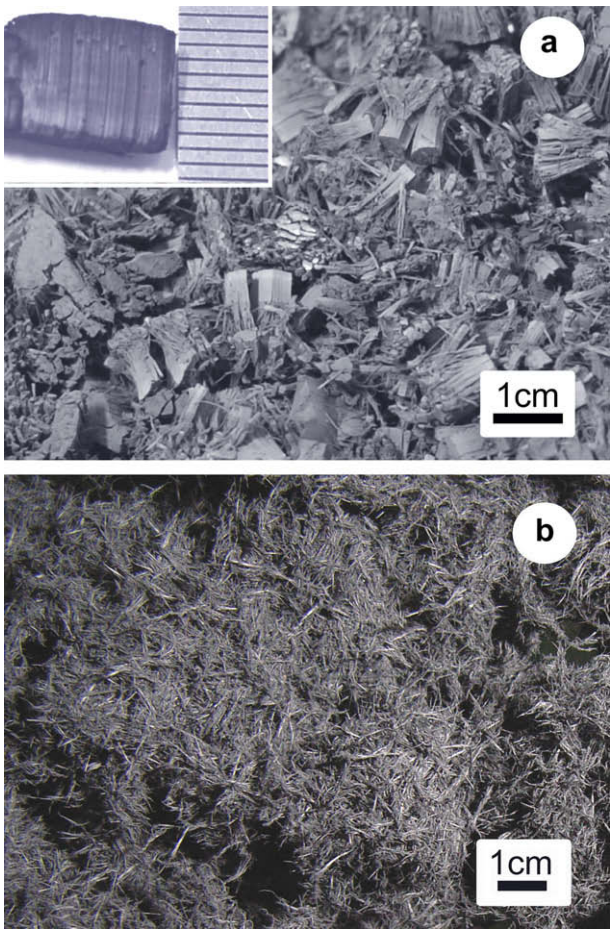
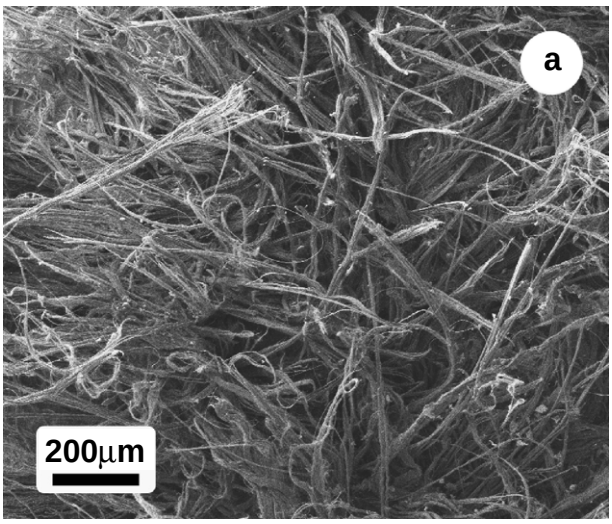


Fig. 1 – Photographs of (a) an initial super long VACNT array, and (b) fluffy CNTs.

both the apparent density and the bundle diameter decreased quickly. When shearing time increased, the rate of decline slowed down. When the shearing time exceeded 300 s, the fluffy CNT diameter maintained at approximately 4 ~ 10 μm, while the apparent density was approximately 3.9 g/L. The CNTs still showed good graphitization (Fig. S11), similar defect densities (Fig. S12) and purities (Fig. 13) to those in the initial arrays. The fluffy CNTs were very flexible and easily distorted.

The initial alignment of CNTs was crucial in obtaining fluffy CNTs by shearing. The agglomerated CNTs, where the CNTs are entangled with each other, are powders with a size of 10 ~ 300 μm. After shearing, the CNTs took on a spherical shape with the sizes distributed from 1 to 10 μm, as shown in Fig. 3. The CNTs were randomly distributed in the initial multi-stage CNT agglomerate structure. During shearing, the multi-stage structure was broken and the CNTs further entangled into CNT spheres. In this study, the CNTs in the array exhibited good alignment compared with the agglomerated CNTs. CNTs in the array showed an anisotropic connection along the CNT radial direction where weak connections existed. On the other hand, the CNTs were strong in the axis direction. Thus, when the arrays were sheared, they were torn into pieces along the axis direction. The pieces were smaller after prolonged shearing. As a result, fluffy



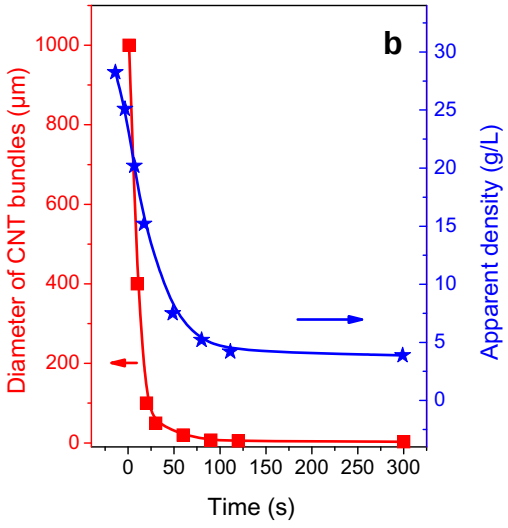


Fig. 2 – (a) Morphology of fluffy CNTs; (b) apparent density and bundle diameter versus shearing time.

CNTs were obtained by shearing the VACNT array while spherical CNTs formed through shearing agglomerates CNTs. When CNT bundles in fluffy CNTs were subjected to the 0.5 mm thick rotor, it can hardly been torn further into smaller pieces. Even if the rotor hit the bundle, the shock might have been relaxed by bundle torsion due to the flexibility of CNT bundle. Consequently, the smallest size of CNT bundles in fluffy CNTs obtained by shearing depended on several factors, such as rotor size, rotation rate, and amount of fluffy CNTs in the shearer. Further studies are required to quantifiably determine the exact size distribution of fluffy CNTs.

Fluffy CNTs are a type of special particle wherein CNT arrays are dispersed into CNT bundles. When fluffy CNTs were placed in a fluidized bed, gas passed through the pores in the fluffy CNTs. The size of pores among CNT bundles increased due to their flexibility and the volume increased accordingly. When the gas velocity increased, so did the volume of fluffy CNTs. However, because of its large size and connection among CNTs bundles, the fluffy CNTs were expected to be

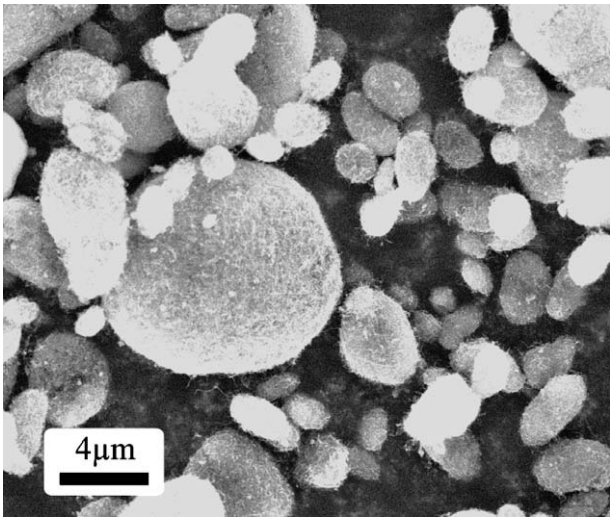


Fig. 3 – Morphology of agglomerated CNTs after shearing.

choked in the fluidized bed. Most of these bundles remained in the reactor because large clusters formed even when the gas velocity was very high. Only some small CNT bundles which did not entangled with large CNT cluster in the fluidized bed were brought out. This indicated that there were weak connections between CNT bundles, and that they could construct conductive net in the gas phase, taking advantage of their large size and good conductivity. Furthermore, the fluffy CNT can be converted into CNT pulp, CNT paper and CNT composite film in another report [11].

Fluffy CNTs, which were composed of CNT bundles with several micrometers in size and of an apparent density of 3 – 10 g/L, were directly obtained through simple high-speed shearing of a VACNT array. There was no noticeable change in the length of CNTs while, an obvious difference existed in terms of macroscopic morphology. It was also confirmed that a key element for fluffy CNT formation was the weak connection determined by the alignment in the initial arrays. The strong anisotropic connection, especially the different connections along the axial and radial directions of the array, resulted in the array being sheared into bundles during high-speed shearing. After 60 s of shearing, the bundle size and apparent density reached about 3 μm and 4.0 g/L, which can be attributed to rotor size, speed, and other factors. It was determined that fluffy CNTs can form a large cluster in a confined space. Meanwhile, fluffy CNTs can be regarded as a type of CNT dispersion in gas, thus providing an important intermediate for functional materials and construction of composites in the future.

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Appendix A. Supplementary material

A video and illustration of fluffy CNTs obtained from a VACNT array, SEM images, transmission electron microscopy images, Raman spectra, and thermal gravimetric analysis curves, are provided. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carbon.2008.10.052.

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Effect of crystalline filling on the mechanical response of carbon nanotubes

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ABSTRACT

The electrical and mechanical properties of the same hybrid carbon nanotube before and after removal of the core Ga-doped ZnS semiconductor filling have been analysed inside a transmission electron microscope (TEM) using a conductive atomic force microscope – TEM system. It is found that the encapsulated material can substantially change the mechanical response of the turbostratic carbon tube container. Furthermore, because the extent of filling is operator-controlled, this provides a simple way to change on-demand the stiffness of hybrid carbon nanotubes.

The advent of nanotechnology has motivated crucial advances in characterisation methods with high spatial resolution. One such technique is transmission electron microscopy (TEM) where developments have not only been made in spatial and energy resolutions but also in the integration with complementary analytical techniques. This has led to

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