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Long super-bundles of single-walled carbon nanotubes

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200 nm-thick super bundles showing a novel polygonization and densely aligned arrangement are found in long single-walled carbon nanotube (SWNT) strands prepared by the vertical floating catalytic method.

Nowadays, researchers are aiming to increase the scale of nanotube manufacturing and make the process less expensive,[1] and one challenge is how long carbon nanotubes can be made. Pan *et al*. reported first the synthesis of 2 mm long arrays of aligned multi-walled carbon nanotubes (MWNTs).[2] For single-walled carbon nanotubes (SWNTs), one school of thought is that the nanotubes are intrinsically short and agglomerate into longer tubes and bundles during production. Our recent work indicated that long (> 20 cm) individual SWNTs can be formed in the vertical floating catalytic condition with subsequent coalesce in strands.[3] Due to the intrinsical length and structural integrity of the long SWNT strands, they showed unique electronic, mechanical and chemical properties. It is expected that they can be used widely in applications for gas storage, composites, quantum wires, electron devices, catalyst carriers, *etc.* Recently, Kim *et al.* reported the synthesis of very long isolated SWNTs (lengths up to 0.6 mm) with loop and closed ring structures.[4] They have revealed that the high yield and natural abundance of semiconducting SWNTs can lead to their use as field effect transistors and sensors.

In this communication, we report novel densely bundled structures (super bundles) found in our long SWNT strands. This type of long strands was synthesized also by our vertical

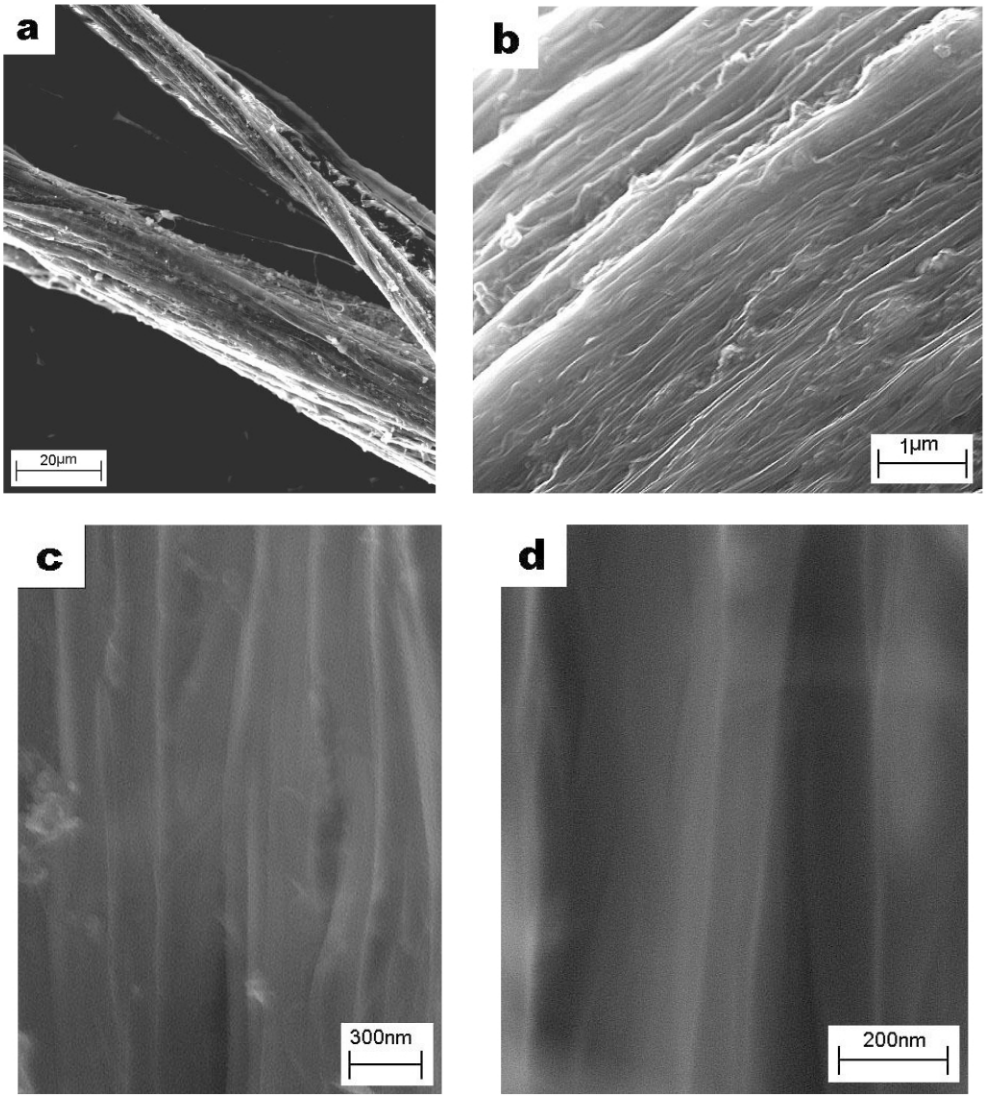

Fig. 1 SEM images of long nanotube strands. (a) A low-resolution SEM image of a long strand; (b) and (c) show the dense arrangement and alignment of the super bundles; (d) shows a side view of polygonal bundle.

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device[3,5] under similar conditions used to produce conventional long SWNT strands.[3] *n*-Hexane was used as the hydrocarbon liquid, and a small amount of thiophene was employed as a sulfur additive. A given composition of ferrocene (0.025 g mL^{-1}) was introduced into the reactor at a higher rate (0.6 mL min^{-1}) than previously employed after heating the reactor to a specified pyrolysis temperature (1473 K). Hydrogen was the carrier gas and was allowed to flow at a rate of 200–250 mL min^{-1}. Our synthesis method needs only a simple setup (only a furnace) and does not require preformed substrates. When increasing the addition of thiophene (0.6 wt%) and the introduction rate of the solution, thicker strands (~1 mm) are found in the as grown materials with a average length of 20 cm. They also appear to have better macroscopic flexibility than previously prepared SWNT strands.[3]

Fig. 1 shows four scanning electron microscope (SEM) images of the long nanotube strands under different resolution. Microscopic branch structures can be observed clearly in Fig. 1(a). In Fig. 1(b) and (c), large (~200 nm thick) aligned nanotube bundles with dense arrangements are evident and exhibit good alignment even at high resolution (Fig. 1(c) and (d)). Some bundles show a novel polygonization (Fig. 1(d)) and a simple geometric model is proposed in Fig. 2. We expect that the super bundles have a hexagonal cross section.

Fig. 3 is the transmission electron microscope (TEM) image of a thinner bundle (~70 nm), showing good tube-alignment and high purity in the super bundle. The SWNT diameter is about 1.4 nm based on the high resolution measurement. In addition, the diameter of SWNTs can be determined by the frequency of the breathing modes from 100 to 300 cm^{-1}. There are two clear peaks of the breathing mode observed (167.51, 175.44 cm^{-1}), showing our SWNTs have a narrower diameter distribution from 1.4 to 1.5 nm, which is slightly different from that of previously produced long SWNT strands.

We believe sulfur is an important element for SWNT formation, even for the formation of super bundles in long strands. Cheng *et al.* has pointed that thiophene can greatly increase the yield of their SWNT ropes.[6] S addition may also be the key controlling factor for the synthesis of our super bundles.

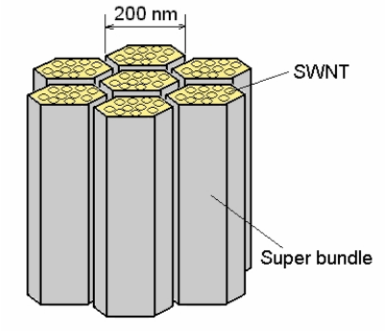

Fig. 2 A simple model of the super bundles.

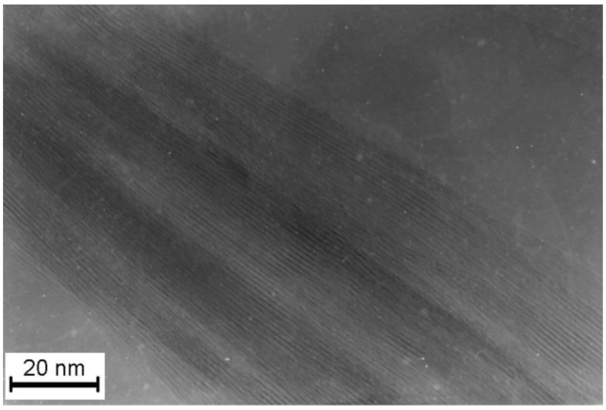

Fig. 3 TEM image of a super bundle. A thinner bundle was selected in order to make the individual SWNT clearly seen.

In addition, the higher amount of ferrocene used gives more opportunities for SWNT nucleation. Under this condition, the flow of hydrogen gas leads to a temperature and concentration gradient, which drives carbon atom diffusion rapidly over and though the metal, to a location where SWNTs assemble into an ordered structure at 1473 K. Indeed, similar structures were found also in long SWNT strands reported previously,[3] which indicated that the conditions in some area meets the need for the formation of super bundles.

Our super bundles in the long SWNT strands are more well-aligned and condensed than Cheng's SWNT ropes[6] and Gennett's super bundles.[7] They would be considered to be good candidates as macroscopic cables because of their mechanical properties as well as their interesting anisotropic electronic, optical and other properties.

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