

Acknowledgements

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Polymerization of short single-walled carbon nanotubes into large strands

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Single-walled carbon nanotubes (SWNTs) have attracted much interest in recent years because of their unique structural, mechanical, and electronic properties, as well as potential applications in nanotube-reinforced materials,

nanoelectronic devices, field emitters, and probe tips for SPM, etc. [1–5]. For most applications a major challenge is how to get nanotubes on a macroscopic scale which have a practical value. Several attempts have been made to do this, such as the formation of SWNT superbundles, and self-assembly of SWNT ribbons using arc plasma or under ambient pressure [6,7]. Important progress was recently achieved by Poulin et al. [8]. They demonstrated that

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SWNTs were assembled into indefinitely long ribbons and fibers by dispersing the nanotubes in surfactant solutions, and recondensing them in the flow of a polymer solution and a microtube mesh was formed. In the present study, we report the chemical polymerization of short carboxylic SWNTs into large strands with the assistance of 1,3-dicyclohexylcarbodiimide (DCC).

The raw SWNT soot was prepared by simple CVD in a tube furnace with gas flow control [9]. In a typical growth experiment, ~500 mg of catalyst were put into an alumina boat inside a quartz tube and were heated to a temperature of 850 °C under argon atmosphere at a flow rate of 250 sccm. Methane flow was introduced at a flow rate of 50 sccm for 5 min and then the temperature was reduced to room temperature. Argon flow was maintained for the duration of the preparation. The catalyst (support and metal particles) was removed first by sonication in 37 wt.% hydrochloric acid for 30 min, and then diluted with de-ionized water and filtered on a $\phi 0.1 \mu\text{m}$ Supor Membrane Disc Filter (Gelman). After that, the obtained SWNT soot was heated in air for 1 h at 500 °C in order to oxidize any amorphous carbon.

Polymerization of SWNTs was performed as follows: the purified SWNTs were oxidized in $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ (4:1 by volume) for 0.5 h. Subsequently, the oxidized SWNTs were dispersed in dimethylformamide (DMF) and then an excess amount of DCC was added. The mixture was stirred overnight at room temperature. After centrifugation, the pale brown-colored supernatant was decanted. The remaining solid was then washed with isopropyl alcohol four times to remove the excess DCC. The resulting black solid was collected by a $\phi 0.1 \mu\text{m}$ Supor Membrane Disc Filter (Gelman), washed with ethanol, and dried at room temperature under vacuum.

The morphology and microstructure of the SWNTs were characterized using atomic force microscopy (AFM) in the tapping mode and field-emission scanning electron microscopy (SEM) at 25 kV. Raman characterization was conducted on a Renishaw System 1000 Raman imaging system equipped with a 632.8 nm, 25 mW He–Ne laser and a CCD detector. The IR spectrum was obtained using a Nicolet AVATAR-360 Fourier transform infrared (FTIR) spectrometer.

In our CVD preparation, we have succeeded in producing short lengths of nanotubes by controlling the growth time, and found that with the same purification procedures, short SWNTs were obtained with higher purity than for the long ones. Fig. 1a shows a typical AFM image of the purified SWNTs grown for 5 min. It can be seen that the resulting SWNT products are preferentially present as individual tubes and/or small bundles, 0.5–1 μm in length, which are randomly oriented. The purification process seems to have thoroughly removed the non-nanotube carbon fractions and metal particles in the products.

Fig. 1b shows Raman spectra of SWNT samples before

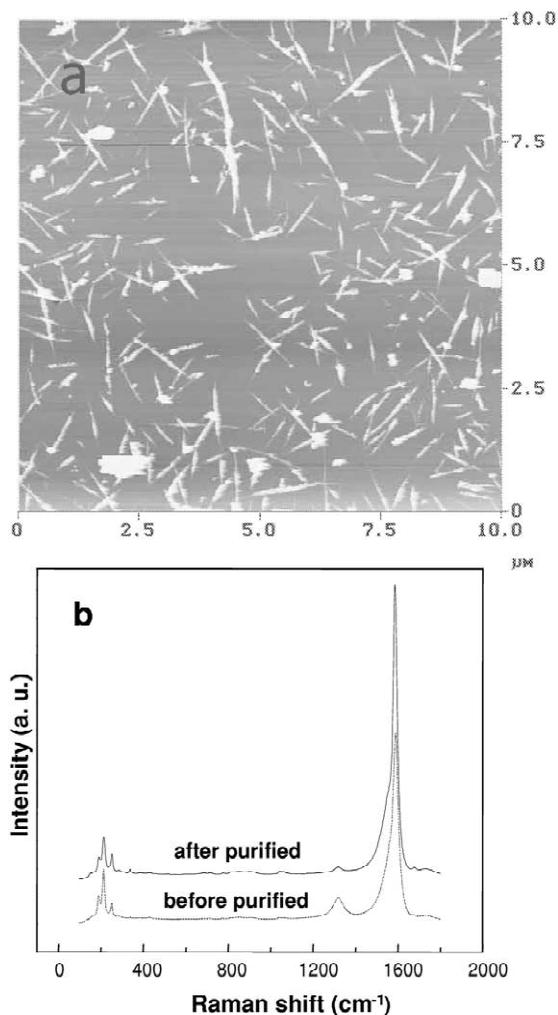


Fig. 1. AFM image of the purified short SWNTs (a) and Raman spectra of SWNT samples before and after the purification process (b).

and after purification. Typical SWNT features are observed for the tangential and radial breathing modes near 1600 and 200 cm^{-1} , respectively. It can be seen that there is also a small band located around 1320 cm^{-1} in the spectrum of an SWNT sample before purification. This result suggests that the product consists of high-purity SWNTs after purification. The radial breathing mode present near 200 cm^{-1} is directly related to the diameter of the SWNTs and the relationship between them can be estimated from the formula $\omega = 223.75/d$, where d is the diameter of the nanotubes and ω is the frequency of the radial breathing mode in wavenumbers [10]. According to this formula, the peaks present at 192, 216, and 254 cm^{-1} correspond to SWNTs with diameters of 1.16, 1.04, and 0.88 nm, respectively. Based upon the above results, we may conclude that the preparation of short SWNTs by our

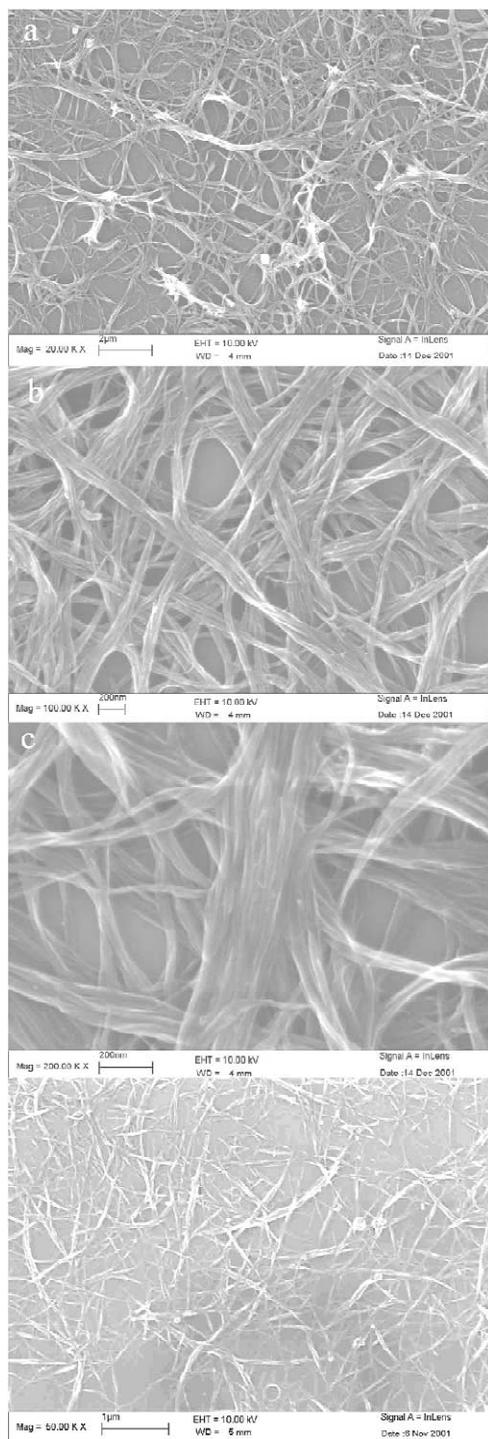


Fig. 2. SEM image of the SWNT strands at different magnifications and different area (a–c), of the purified SWNTs after polymerization using DCC (d).

method is effective and advantageous. On the one hand it avoids longtime sonication treatment in strong acids and oxidants which are widely used in the cutting of long tubes and may cause severe damage to small-diameter nanotubes. On the other, this method is easy and can be used to synthesize a large quantity of short SWNTs for further treatments and applications.

Because of their high purity and suitable length it seemed worthwhile to further chemically manipulate these nanotubes. Fig. 2a–c shows typical SEM images of the polymerized SWNTs. It can be seen that the original short thin tubes have aggregated into larger SWNT strands. The resulting strands have a wide distribution of radial sizes. The smallest size is as thin as a few nanometers, while the largest one can reach up to 150 nm (Fig. 2c). Most of the strands have radial sizes in the range 50–100 nm. The lengths of most strands are greater than 20 μm , much longer than the original short tubes. It is interesting to see that some of the tubes are belt-like and are interwoven to form a larger network. The nanotube ribbons are preferentially aligned along the long axis of the bundles and this is maintained over the entire length, although many strands are also twisted relative to each other. So in this sense, we can say that short and thin SWNTs have been polymerized into large strands.

In order to verify that the formation of large strands was caused by the condensation reaction, not by solvent effects, tubes in a DMF solution without DCC were also refluxed but no strands were formed in such a system (Fig. 2d). In return, FTIR investigations provide further evidence on this phenomenon. It is well-known that the oxidation of SWNTs in $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ (4:1 by volume) can introduce a large number of oxygen-containing groups [11], such as carboxylic acid ($-\text{COOH}$), hydroxyl ($-\text{OH}$), and carbonyl (>C=O), at both the ends and sidewalls of the tubes, with

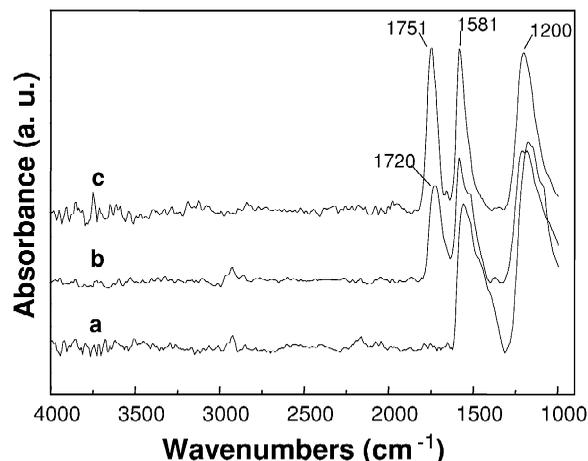


Fig. 3. FTIR spectra of the purified short SWNTs (a), the oxidized SWNTs (b), and the polymerized SWNTs (c).

carboxylic acid groups being predominant. The FTIR results shown in Fig. 3 reveal that the purified SWNTs exhibit two peaks around 1581 and 1200 cm^{-1} (Fig. 3a), which are assigned to the C=C stretch and C–C in-ring stretch of SWNTs, respectively. However, it is obvious that a new strong peak at 1720 cm^{-1} appears in the spectrum of the oxidized SWNTs (Fig. 3b). This indicated that a large number of carboxylic acid groups, as well as other oxygen-containing groups were indeed introduced on the SWNT surface after oxidation in $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$. After the polymerization reaction, the absorption bands of carboxylic acid groups shifted from 1720 to 1751 cm^{-1} which provides evidence for the formation of carboxylate (Fig. 3c), and indicates that the oxidized SWNTs terminated with carboxylic acid were bound to each other by forming carboxylate and intermolecular hydrogen bonds between carboxylic acid groups due to the coupling effect of DCC. This process could be of significant importance for the preparation of carbon nanofibers and nanocomposites with stronger mechanical properties than nanoropes in which the neighboring SWNTs are held together only by van der Waals forces.

In summary, we have reported a simple chemical method which employs 1,3-dicyclohexylcarbodiimide to polymerize the oxidized SWNTs and assemble them into large strands. The results show that the SWNT strands obtained had radial sizes in the range of 50–150 nm and lengths beyond 20 μm . They also have a preferred orientation and tend to align along the axial direction to form large bundles. The easy manipulation of the well-aligned strands offers more opportunities for their fundamental research and applications of SWNTs.

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Carbon nanowires with new microstructures

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The importance of nanomaterials did not really become evident until the discovery of carbon nanotubes (CNT) [1]. Nanomaterials exhibit physical and chemical properties that are different from, and normally much better than, those of the bulk forms. These outstanding properties are

often determined by the microstructure. For example, it is well-known that CNT exhibit metallic or semiconducting properties depending on their microstructure or atomic arrangement [2–4].

CNT, which in general includes carbon nanowires (CNW), are probably by far the most studied nanomaterials. Several one-dimensional nano-carbons exhibiting various structures have been reported in which the graphene planes are arranged in one of three ways: parallel to the

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