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Self-organized Ribbons of Aligned Carbon Nanotubes

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Carbon nanotubes (CNTs) have attracted scientific and technological interest because of their novel properties and potential applications.[1] Their exceptional mechanical, electrical properties suggest that they can be used as field emitters,[2−4] scanning probes and sensors,[5−7] devices in nanoelectronics,[8,9] nanotweezers,[10] and reinforcing materials.[11] Many potential applications require aligned CNTs and great progress has been made on this subject. The first report about aligning the CNTs incorporates them into a matrix and then slices the composites so as to cause nanotube alignment along the direction of cutting.[12] Another method reported is to deposit purified CNTs on a plastic surface and then rub with a Teflon or an aluminum foil to align the nanotubes parallel to the support surface[2]. Recently, aligned nanotube arrays were grown directly by catalytic methods.[13−15] Very recently, Vigolo and co-workers successfully produced macroscopic fibers and ribbons of oriented single-walled CNTs.[16] Here, we describe a simple method to fabricate self-organized long carbon nanotube ribbons at 373 K under ambient pressure.

Multiwalled CNTs, with an average diameter of 30 nanometers and length ranging from hundreds of nanometers to micrometers, were synthesized by the catalytic decomposition of propylene. The as-prepared CNTs were immersed in concentrated nitric acid and hydrofluoric acid for 24 h, respectively, to dissolve the catalyst particles and then were washed with deionized water. After the samples were dried, they were ground by ball milling for 20 min to break up the nanotube clusters. Subsequently, the samples were dispersed in a mixture of concentrated nitric acid and sulfuric acid (5:3 vol ratio) and refluxed for 1 h at 413 K. The samples were extracted several times by vacuum filtration using a ceramic filter until the solution reached a pH value of 7. Finally, the filtered samples were suspended in deionized water at a definite concentration (suitable concentration to form the ribbons is 20−50 mg/mL). The resulted solution was annealed at 373 K in a vacuum oven for 12 h. Long ribbons of aligned CNTs self-assembled on the wall of the container (glass beaker).

The ribbons can be formed in two orthogonal orientations within the container. Figure 1 shows that ribbons can assemble either perpendicular to (a) or parallel to (b) the bottom of the container. When a vacuum was applied to the beaker placed in a vacuum oven at 373 K, the ribbons would assemble on the walls perpendicular to the bottom of the beaker (Figure 1a). Note that the vacuum should be kept at several tens of mTorr (about 10 mTorr in our experiments); high vacuum would lead to a nanotube solution overflow from the beaker during evaporation of water. If no vacuum is applied, the ribbons will organize on the beaker wall, parallel to the bottom of the beaker (Figure 1b). When the ribbons grown perpendicular to the container are peeled off from the beaker wall, the bent ribbons become straight due to the pre-stress formed during the self-organization of the aligned nanotubes in the ribbons. The ribbons are about 50−100-μm wide, 4−12-μm thick, and 100-mm long. The mean density of the ribbons is 1.1 g/cm^3. Most metallic particles are removed by the dispersion of the tubes in nitric acid and hydrofluoric acid for 24 h prior to boiling.

Figure 2 shows typical scanning electron microscopy (SEM) images of the nanotube ribbons. The geometry of the ribbon is extraordinarily regular, with a rectangular cross section as shown in Figure 2a. The dimension of the cross section varies according to the nanotube concentration in solution and the evaporation time. Thinner ribbons could be obtained by decreasing the nanotube concentration and/or by increasing the evaporation time, which allows for further optimization of the nanotube self-organization process. Figure 2b demonstrates a bent ribbon, showing flexibility of the fabricated nanotube ribbon along the ribbon axis. The nanotube alignment can be identified easily from the external surface of the ribbons, as shown in Figure 3.

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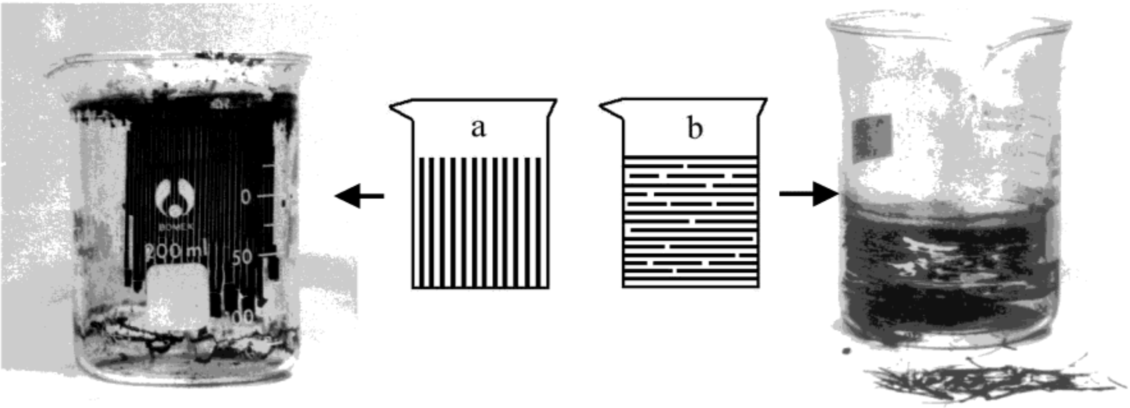

Figure 1. Photographs of beakers and schematic diagrams showing the growth direction of the nanotube ribbons. (a) Perpendicular to and (b) parallel to the bottom of the beaker.

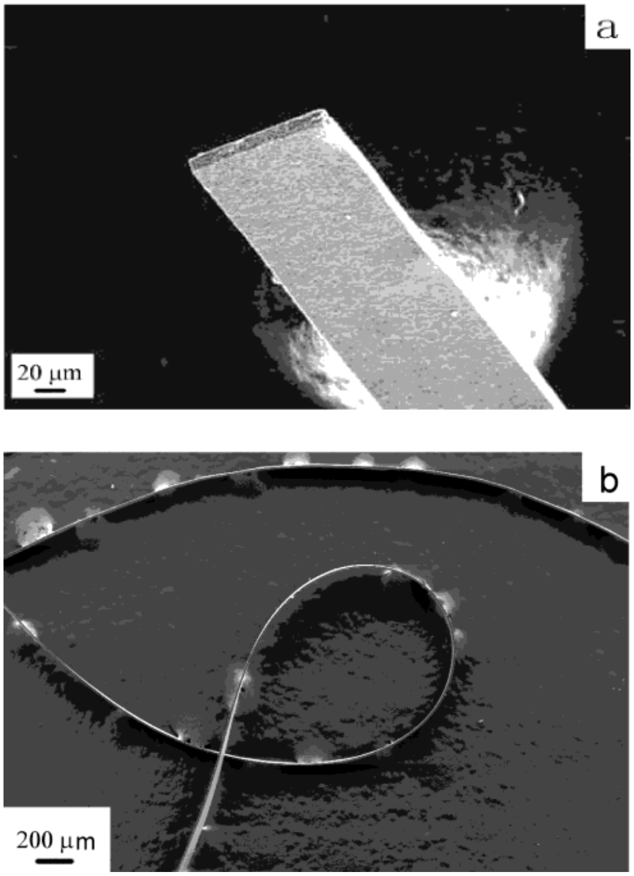

Figure 2. SEM images of a ribbon that consists of aligned carbon nanotubes. (a) Cross section of the nanotube ribbon. (b) Bent ribbons.

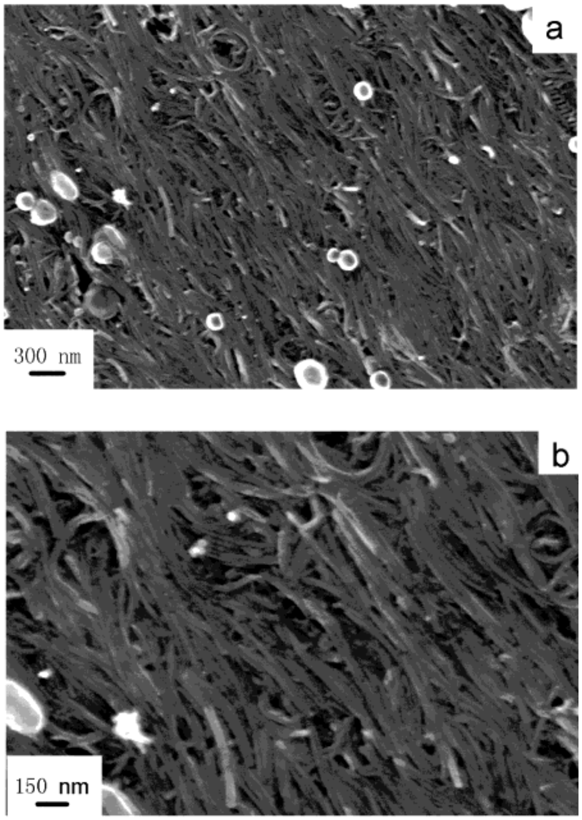

Figure 3. (a) SEM image of the surface morphology of a nanotube ribbon showing the alignment of the nanotubes. (b) Higher magnification image of (a).

The ribbons show bundled structures along the longitude of the ribbons, although a few appear to be woven in the lateral direction.

The self-organization of the aligned nanotube ribbons might be related to two factors: prolonged heating of the solution (373 K) and refluxing of the sample with the acid. Heating the solution may provide the driving force for alignment of the nanotubes. This can be confirmed by the fact that high-density well-aligned ribbons could be obtained by increasing the evaporation time. Without refluxing the samples with an oxidizing acid, the ribbons cannot self-assemble. It is known that the chemical oxidation of carbon materials is frequently used as a method to obtain a more hydrophilic surface structure with a relatively large number of oxygen-containing surface groups. These oxygen-containing groups behave as acids or bases, which possess ion-exchange properties and improve the dispersibility.[17] Previous reports[18,19] that referred to the oxidation of CNTs with nitric acid and sulfuric acid suggest introduction of many functional groups, such as hydroxyl (−OH), carboxyl (−COOH), and carbonyl (>C=O), on the surface of CNTs. The nature of the as-prepared and oxidized CNT surface groups was characterized by infrared spectroscopy (IR)(Figure 4). The as-prepared CNTs exhibit two peaks at ca. 1550 and 1200 cm^{-1},

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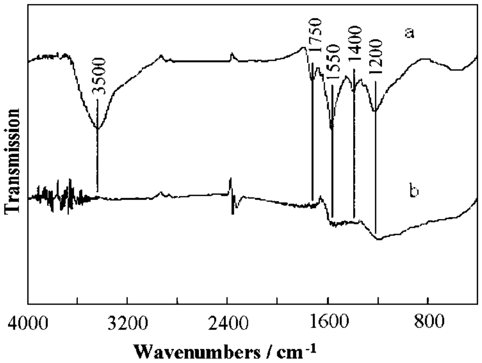

Figure 4. Infrared spectra of (a) oxidized CNTs with acids and (b) as-prepared CNTs.

which might be assigned to the carbon skeleton.[18] These two peaks become sharper after the CNTs are oxidized. The signature of >C=O functional groups is evident at 1750 cm^{-1} and −OH functional groups appear at 3500 cm^{-1} after oxidation. The peak at 1400 cm^{-1} is associated with O−H bending deformation in carboxylic acids and phenolic groups. It is obvious that there are many more functional groups connected to carbons on oxidized CNTs. These functional groups can not only stabilize the nanotubes at much higher concentrations[18] but also play a bonding role between the CNTs to form the ribbons. It was confirmed that the as-prepared CNTs could not form these ribbons. When they were dried at 373 K, the nanotubes would come in mutual contact through deformation caused by surface tension and through the binding of the functional groups. In addition, due to the high density of the aligned nanotubes and high surface area of nanotubes, the van der Waals forces between them might be another main interacting force for the processed nanotubes.

The long aligned carbon nanotube ribbons may have many potential applications. For instance, their electrical resistivity was measured using a four-probe method. The resistivity of the ribbons at room temperature is about 9.7 $\mu\Omega$m, indicating a good connection between the nanotubes. They are so long and flexible that they can be woven into networks to be used as electronic cables or incorporated into composite materials. The hardness value measured on the ribbon corresponds to 4.47 GPa, although no strength measurement could be performed due to the brittle nature of the ribbons. Further studies are currently underway to explore the mechanical, thermal, and magnetic properties of the ribbons.

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