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Fibers of carbon nanotubes

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ABSTRACT

We briefly review some methods recently proposed to make films and fibers of preferentially oriented carbon nanotubes. We discuss in more detail a simple spinning process which consists in dispersing the nanotubes in a surfactant solution, re-condensing the nanotubes in the flow of a coagulating polymer solution to form a nanotube mesh, and then collating this mesh to a nanotube fiber. We measure the mechanical properties of the obtained fibers and characterize the nanotube alignment along the fiber axis by X-ray scattering experiments. We show that the alignment can be improved by stretching the fibers under well-defined conditions. This allows the Young's modulus to be increased by a factor 4, leading thereby to materials forty times stronger than high-quality buckypaper. We believe that these improved fibers can already be potentially useful as functional materials. A simple example of electromechanical actuation is shown.

INTRODUCTION

Single wall carbon nanotubes (SWNTs) are considered as very promising systems to make functional materials [1-3]. Unfortunately, as produced nanotubes are under the form of a light, fragile and isotropic soot [4,5]. This soot is of rather difficult use and far from being optimized. Processing and assembling nanotubes on macroscopic scales to obtain materials of more practical use is thus an important issue. Thin mat, known as bucky paper, can be obtained by drying SWNTs suspensions onto membrane filters [6]. Although classical bucky papers are almost isotropic, they are widely used to characterize the properties of nanotubes on macroscopic scale and to make functional systems mostly comprised of nanotubes [7]. We do not consider in this paper composite materials that include only a relatively small fraction of nanotubes, generally embedded in polymeric matrices. Recent progresses have shown the possibility to make films of aligned nanotubes by using high magnetic fields [8-10] and to make fibers of aligned nanotubes by using an electrophoretic process [11,12] or by directly spinning an aqueous suspension [13]. We briefly review in this paper the two first processes and focus on the fibers obtained by the last spinning process. This method consists in dispersing the nanotubes in a surfactant solution, re-condensing the nanotubes in the flow of a coagulating polymer solution to form a nanotube mesh, and then collating this mesh to a nanotube fiber. We measure the mechanical properties of obtained fibers and characterize the nanotube alignment along the fiber axis by X-ray scattering experiments. The alignment can be improved by stretching the fibers under well-defined

conditions. This allows the Young's modulus to be increased by a factor 4, leading thereby to materials more than ten times stronger than high-quality bucky paper. We believe that these improved fibers can already be potentially useful as functional materials. A simple example of electromechanical actuation is shown.

FILMS AND FIBERS OF ALIGNED NANOTUBES

Magnetically aligned materials

Classical films of buckypaper [6] are made by deposition from suspensions onto a membrane filter. In ordinary materials, nanotubes bundles lie preferentially in the plane of the film but they are randomly oriented within this plane. When dried in a high magnetic field (several Tesla), Walters et al. [10] have achieved a preferential orientation of the nanotubes in the plane of the film. The used nanotubes are under the form of bundles organized as a two-dimensional hexagonal array perpendicular to the bundle axis. The crystalline nature of the bundles has been used to quantitatively probe their degree of alignment in the films using electron and X-ray diffraction. Mosaic distributions are obtained from the azimuthal intensity distributions of the first diffraction peak of the hexagonal lattice. The full width at half maximum (FWHM) deduced from Gaussian fits ranges typically between 25° and 35°. Hone et al. [9] have reported quantitative measurements of the anisotropic electrical and thermal transport properties of magnetically aligned nanotubes. Both electrical and thermal conductivities are found to be significantly higher along the H-alignment axis. Although it cannot be routinely used because of the needed high magnetic fields, this method is currently one of the most promising to achieve pronounced alignments and improved properties of nanotubes assemblies.

Fibers made by an electrophoretic method

Gommans et al. [11] have developed a simple method to make SWNTs fibers that posses a substantial alignment. The authors have characterized the degree of alignment with polarized Raman spectroscopy.

The first step of the method consists in dispersing nanotubes in an organic solvent. A classical carbon fiber is attached to a conducting wire coupled to a motor-driven translation stage. This carbon fiber, used as an electrode, is translated along its axis down in the nanotube suspension to a depth of few mm. The carbon fiber is slowly withdrawn from the suspension in the presence of an applied voltage. As it pulls out of the liquid, a nanotube fiber, attached to its end, forms spontaneously from the suspension. The obtained nanotube fibers are several centimeters long and their diameters range typically between 2 and 10 microns depending on the conditions. A detailed analysis of the nanotube alignment within the fibers has been achieved using polarized Raman spectroscopy [11,12].

In reference 11, the authors considered a certain fraction p of nanotubes uniformly distributed within an angle Θ about the fibers axis, and the rest $(1\text{-}p)$ distributed over the other angles. From the ratios of Raman peak intensities as a function of the fiber axis orientation, it was deduced that p is about 0.86 and Θ about 31°. This means that 86% of the nanotubes are distributed within ± 31° about the fiber axis. More recently, Hwang et al. [11] have proposed a more quantitative analysis by fitting the Raman intensity versus the angle between the fiber axis and the polarization direction with a Lorentzian form. The FWHM of the distribution was found to

be 23°, showing that this method is also allowing macroscopic assemblies of oriented nanotubes to be produced.

SPINNING PROCESS FOR MAKING NANOTUBES FIBERS

This last process [13], reminiscent of the so-called wet-spinning process of industrial polymer fibers, is particularly simple and potentially scalable for large production. The method consists in dispersing the nanotubes in a surfactant solution, re-condensing the nanotubes in the flow of an adsorbing polymer solution to form a nanotube mesh, and then collating this mesh to a nanotube fiber by pulling it out of the solvent. The water drains and evaporates leading to the collapse of the mesh into a dry fiber. It is a few tens of cm long and its diameter can be varied between 10 and 100 □m. If necessary, the polymer and remaining surfactants can be removed by washing the fibers with pure water and by annealing them at high temperature so that one can obtain fibers mostly comprised of nanotubes [14, 15]. The degree of alignment in raw fibers of nanotubes bundles made by the electric arc method [5] has been characterized by X-ray diffraction [15]. An angular scan at constant $Q \approx 0.4 Å^{-1}$, the wave vector which corresponds to the position of the (1,0) peak of the SWNT bundles, exhibits maxima of scattering perpendicular to the fiber axis, which shows that the SWNT bundles are preferentially aligned along this axis. The peak width, deduced from a Gaussian fit, characterizes the orientations of the NT bundles in the fiber (together with their possible curvatures). For raw fibers made in the conditions of reference 13, we find that the FWHM (Full Width at Half Maximum) ≈75°. We have tested fibers made in other conditions and have observed that the spinning conditions do not strongly affect this value. The Young's modulus of the raw fibers has been measured and was found to vary between E=7 and 15 GPa, depending on the batch of raw nanotubes. Although far weaker than the Young's modulus of individual nanotubes, this modulus is already an order of magnitude higher than that of high quality non-aligned nanotube paper [7]. Nevertheless, the alignment in raw spun fibers is still far from a perfect alignment and one might expect better properties from more aligned materials.

We report in this paper an efficient post-preparation stretching procedure based on the surprising elastic deformability of, non-annealed, fibers that are rewetted in an appropriate solvent. After coagulation and collation of the initial mesh, the fibers form an interconnected of nanotubes and adsorbed polymers. If the obtained fibers are not annealed they can be swollen and become easily deformable in a solvent that has a rather good affinity for the coagulating polymer. Surprisingly, even in a solvent in which the polymer is highly soluble, the polymer-nanotube network fibers don't disassemble. By contrast to classical composite fibers that would decompose in a good solvent of the polymer matrix, the present fibers are still strong enough to sustain a significant tensile stress and be twisted or stretched without breaking. This is achieved by simply loading the fiber with a weight at the end of the fibers. The fibers are then drawn out of the solvent and dried under tensile load. They can also be twisted and dried with an imposed torque that maintains the twist during the drying. As shown in the scanning electron micrographs of figure 1, this strongly modifies the aspect of the obtained fibers.

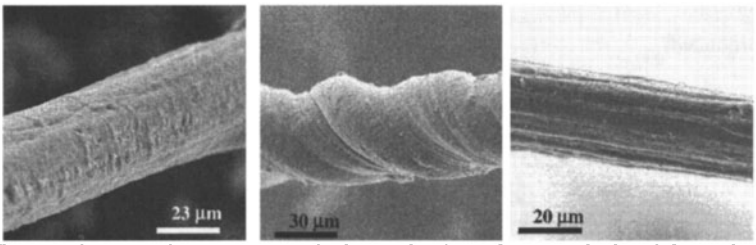

Figure 1. *Scanning electron micrograph of nanotubes fibers. Respectively, from left to right: a raw, a twisted and a stretched fiber.*

The fibers studied in this work are prepared using the following conditions. An homogeneous SWNT aqueous suspension is obtained by sonicating a mixture comprised of 1,2%wt of sodium dodecyl sulfate (surfactant) and 0,5%wt of SWNT (nanotubes made by the electric are method [5]). This suspension is injected through a cylindrical spinneret (diameter 0.5 mm) at a rate of 100ml/h in the laminar stream of a coagulating polymer solution flowing at 360 m/h. The polymer solution is comprised of 3%wt of polyvinyl alcohol (PVA, Mw 100 000 or Mw 50000), an adsorbing polymer that induces the coagulation of the nanotubes through bridging flocculation [16]. As a result, a mesh made of adsorbed PVA and carbon nanotubes is obtained. This mesh pre-fiber is washed and rinsed several times with pure water in order to remove most of the surfactants and polymers. Then, it is collated and dried by simply pulling the mesh out of water. The diameter of the fibers is about 35microns. These fibers are then immersed in water and loaded with different weights. As shown in figure 2, the fibers can be stretched up to 160% with a weight of about 650mg, which corresponds to a tensile stress of about 7 Mpa.

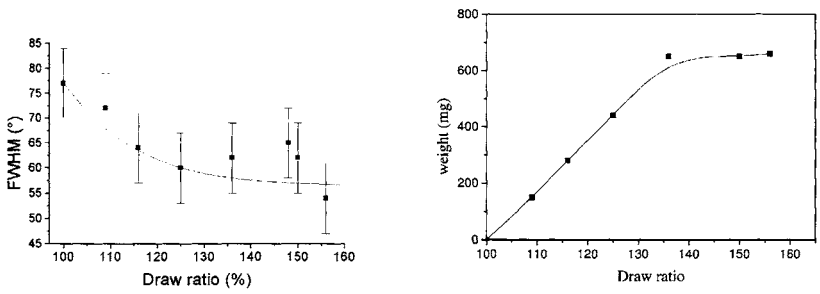

Figure 2. *The graph on the left shows the FWHM as a function of the draw ratio, for fibers wetted with water and dried under tensile load. The graph on the right gives the applied masses for the different draw ratios. Solid lines are guides for the eyes.*

The fibers are then redried under tensile load and studied by X-ray scattering. The results in figure 2 show a substantial improvement of the NT orientations in stretched fibers, with FWHM down to 50°. However, the procedure is only efficient for drawing ratios smaller than 125%. For higher drawing ratios, the FWHMs and the applied stress are constant (see right graph in figure 2). This observation presumably reflects some sliding motion of the SWNT bundles inside the fiber.

Experiments in other solvents are currently in progress to circumvent these difficulties. We can indeed expect a stronger adsorption of the polymer chains in a poorer solvent of the polymer and thus less sliding effects and more cohesion of the nanotubes-polymer network.

Mechanical tensile tests have revealed a very important consequence of the improvement of the SWNT orientation. The Young's modulus of stretched fibers can be increased by a factor 4, as shown in figure 3. The modulus of the strongest fibers we have obtained is about 40GPa, which is 40 times higher than the modulus of high quality bucky paper.

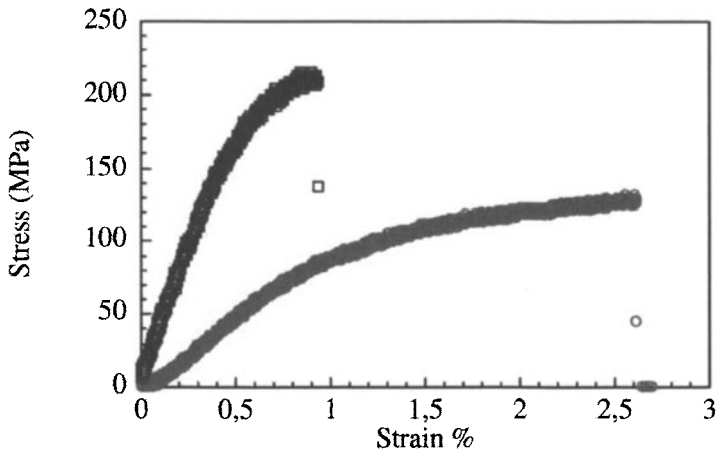

Figure 3. *Stress vs strain curves of dried nanotubes fibers. The lower curve (circles) shows the behavior of a non-stretched fiber. Its Young's modulus, deduced from the slope of the curve at low strain, is about 10GPa. The upper curve (squares) shows the behavior of a stretched fiber. Its Young's modulus is about 38GPa.*

Since bucky papers have been already shown to be useful to make functional materials [7], we can anticipate that the present fibers could exceed performances already reported for nanotubes systems. Preliminary experiments along this direction have been initiated. Current experiments are in progress to test our fibers as highly conducting textile and as actuators. A simple demonstration of an electromechanical actuation effect is illustrated in figure 4. It shows a nanotube fiber coated on one side with a polymer gel. This gel, in contrast to the nanotubes, does not respond to the external field. This system forms a simple bimorph device, similar to those made with buckypapers [7], which deforms under an applied voltage between the fiber and an electrode immersed in an electrolyte solution. The actuation is based on the capability of the nanotube fibers to expand and contract upon charge injection when a voltage is applied between the fiber and the electrolyte solution.

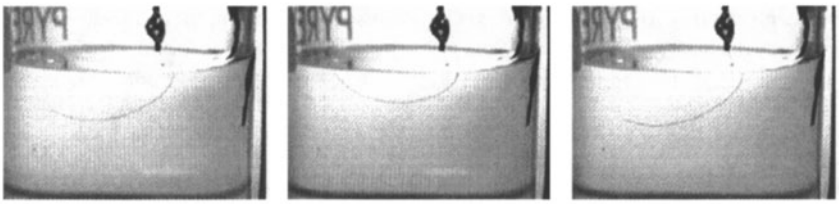

Figure 4. *Electromechanical actuation of a SWNT fiber in an electrolyte solution (NaCl 1M) when an AC voltage of 1V is applied at a frequency of 1Hz. To make a simple bimorph device, the fiber is coated on one side with a polymer gel that doesn't respond to the applied voltage. In contrast, the nanotubes expand and contract upon charge injection as described in reference 7. As a result the bimorph exhibits a periodic motion as shown in the pictures.*

CONCLUSION

We have described recent progresses in making optimized carbon nanotubes assemblies. The obtained materials contain preferentially oriented SWNTs and are encouraging for the use of SWNT on macroscopic scale as functional materials. The spinning process described in more details in this paper lead to systems that are oriented. This can be improved by using a simple post-preparation stretching process. This method is based on the elastic deformability of swollen networks of nanotubes and adsorbed polymers. It allows the mechanical properties of the obtained fibers to be improved by a factor 4. Further characterizations, including measurements of transport and electromechanical properties, are in progress. From preliminary results we already know that these fibers can be used to make functional materials such as actuators and electrically conducting fibers or textiles. In addition, considering the simplicity of the spinning and stretching process, we believe that the experiments described in this work could be scaled up for larger productions.

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Micropatterned Vertically Aligned Carbon Nanotube Growth on a Si Surface or inside Trenches for field-emission devices

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ABSTRACT

The good field-emission properties of carbon nanotubes coupled with their high mechanical strength, chemical stability, and high aspect ratio, make them ideal candidates for the construction of efficient and inexpensive field-emission electronic devices. The fabrication process reported here has considerable potential for use in the development of integrated radio frequency amplifiers or field emission-controllable cold electron guns for field emission displays. This fabrication process is compatible with currently used semiconductor processing technologies. Micropatterned vertically aligned carbon nanotubes were grown on planar Si surface or inside the trenches, using chemical vapor deposition, photolithography, pulsed-laser deposition, reactive ion etching, and the lift-off method. To control the field-emission current by a 3rd electrode, the gate electrode, we grew carbon nanotubes inside the trenches. This triode-type structure is the best to realize the gray-scale carbon nanotube field emission. This carbon nanotube fabrication process can be widely applied for the development of electronic devices using carbon nanotube field emitters as cold cathodes and could revolutionize the area of field-emitting electronic devices such as RF amplifiers and field emission displays.

INTRODUCTION

It is well known that carbon nanotubes have superior mechanical strength and low weight (tensile modulus ~1Tpa)[1], good heat conductance (heat conductivity of MWNT bundles ~1200W/m•K)[2], varying electronic properties depending on their helicity and diameter[3], a large surface area, which is useful for the adsorption of hydrogen or other gases (H_2 can be stored on 98wt% pure SWNTs up to ~7wt%.)[4], and the ability to emit a cold electron at relatively low voltages due to high aspect ratios and nanometer size tips[5]. Therefore, carbon nanotubes have great potential for applications to field emitters for flat-panel field-emission displays[6] and vacuum microelectronic devices such as microwave power amplifier tubes, nano-

FETs[7], nano-Schottky diodes, ion storage for batteries, and mechanical structures requiring low weight and high strength.

There is considerable interest in designing and manufacturing field-emission electronic devices with a small size and low power consumption using arrays of field-emitting diamonds or Mo metal tips. The major problems with these tips are that positive ions, which are formed in the interelectrode gap, sputter off the sharp emitting tips[8] and cause them to become blunt. As a result, the lifetime of the emitting tips becomes shortened. The good field-emission properties of carbon nanotubes coupled with their high mechanical strength, chemical stability, and high aspect ratio, however, make them ideal for the fabrication of efficient and inexpensive field-emission electronic devices. How can regular arrays of carbon nanotubes be created for field-emission tips? A need exists to develop carbon nanotube growth techniques which are compatible with currently used semiconductor processing technologies, in order to achieve the above goal.

In this paper, we describe a carbon nanotube fabrication process, which results in vertically aligned stable field emitter arrays on patterned flat substrates or inside the trenches. To control the field-emission current by a 3rd electrode, the gate electrode, we grew carbon nanotubes inside the trenches. This triode-type structure is the best to realize the gray-scale carbon nanotube field emission. The fabrication process reported here will be of great help in developing integrated radio frequency (RF) amplifiers or field emission-controllable cold electron guns for field-emission displays (FEDs).

EXPERIMENTAL DETAILS

A considerable effort has been devoted to the fabrication of arrays of field emitters world-wide[6, 9-16]. In the process described here, p-type Si(100) wafers with resistivities of 3~6 Ωcm are used as substrates and Fe as a catalyst for carbon nanotube growth. First, in order to achieve a selective micropatterned growth on planar Si substrates, a patterned Fe film was made on Si substrates to attain the desired selective growth of carbon nanotubes. Si substrates were patterned with Fe films with a thickness of 300Å and side lengths of 20μm by 20μm at a pitch distance of 25, 30, or 40μm, by means of pulsed-laser deposition (PLD) and a lift-off patterning method. The advantage of Fe deposition by PLD over other deposition methods lies in the superior adhesion of Fe to a Si substrate due to high kinetic energies of the generated Fe species. To summarize the lift-off method used, a Si substrate was coated with HMDS (Hexamethyldisilazane) to enhance the adhesion between the Si wafer and the PR (photoresist). We then spin-coated the PR on the Si substrate at 4000 rpm for 40 seconds, followed by soft-baking in an oven at 88℃. The PR-coated Si substrate made contact with an optical mask bearing fine patterns and was exposed to light. The PR pattern, obtained after the development, was used as a mask for Fe catalyst deposition by PLD. By dissolving the PR used as a mask in