Assembly of 1D Nanostructures into Sub-micrometer Diameter Fibrils with Controlled and Variable Length by Dielectrophoresis**

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Currently a significant amount of research activity is directed towards synthesis of 1D nanostructures including carbon nanotubes (CNTs) and inorganic nanorods. Several general approaches such as the vapor–liquid–solid transformation process have been developed that are very successful in stabilizing a large number of materials with considerable control in uniformity. The unique geometry and novel properties of the nanotubes and nanorods make them attractive building blocks for new functional materials and devices. Recent experiments have demonstrated their potentials as high-resolution microscopy probes, conducting fibers, and high performance composite fillers. Although considerable progress has been made in the synthesis of nanostructured materials, development in this field in general is hindered by the lack of bottom-up manufacturing processes that can efficiently assemble functional structures and devices using these nanostructured building blocks.

Here we report a dielectrophoresis method to manipulate, align, and assemble 1D nanostructures using alternating current (AC) electric field. Pre-formed CNTs dispersed in water are assembled into micro-electrodes and sub-micrometer diameter fibrils with variable lengths from ~1 μm to over 1 cm. The CNTs within the fibril are bonded by van der Waals forces and are aligned along the fibril axis. The method affords fine control of the fibril length and is capable of parallel fabrication of many fibrils using the same source. The short fibrils can potentially be used as the probes for scanning probe microscopes (SPMs) and the long fibrils as electrodes and conducting wires.

Scanning electron microscope (SEM) images of a single-wall carbon nanotube (SWNT) fibril drawn from the suspension are shown in Figure 1. The fibril is about 100 μm in length and 0.2 μm in diameter. One end of the fibril is anchored to the apex of the W tip. Close examination showed that at the interface individual SWNT bundles adhered on the surface of the W tip and coagulated into a thin fibril comprising of only a few SWNT bundles in the radial direction (Fig. 1b). The surface of the fibril is smooth and the diameter is uniform throughout. Since the SWNT bundles used are ~2 μm in length and 30–50 nm in diameter, the morphology indicates that the SWNT bundles are aligned along the longitudinal axis of the fibril and in the direction of the electrical field. The very end of the fibril comprises only one SWNT bundle as shown by the SEM image in Figure 1d. Except at a few points over the entire length, the fibril surface is remarkably free of nanoparticles, amorphous carbons, and other impurities that are ubiquitously present even in the purified SWNTs.

The diameter of the fibril depends on several parameters such as the drawing rate, the electrical field gradient, the sharpness of the W tip, and the concentration of the suspension. The length of the fibril is controlled by the distance the W tip travels. Turning off the field or withdrawal of the tip at a rate faster than the CNT deposition rate stops the assembly.

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process. By controlling these parameters fibrils ranging from 1 μm to greater than 1 cm were fabricated. Examples of fibrils of different length are shown in Figure 2.

The assembly method has also been applied to other 1D nanostructures including multi-wall carbon nanotubes (MWNTs). The morphology of the MWNT fibril is slightly different from that of the SWNT fibril. Protrusions of individual MWNTs from the surface of the fibril are common. This is attributed to the fact that the MWNTs are not as flexible as the SWNTs and often have permanent kinks. Similar to the SWNTs, the tip of the fibril consists of only one MWNT.

The adhesion between the CNTs and the W tip was tested by applying an electrical field between the fibril and a counter electrode in 10⁻⁷ torr vacuum. No de-bonding was observed at 6–10 V μm⁻¹ electrical field. With further increase of the electrical field, the CNTs break off one segment at a time starting from the very tip of the fibril. This can be utilized as a way to shorten the fibril length after deposition. The strong bonding is attributed to the interfacial morphology. As shown by the SEM images (Figs. 1, 2), the tip of the W electrode is covered with entangled CNTs that coagulate into a fibril. The entanglement and the relatively large contact area give rise to the strong adhesion. The bonding and strength of the fibril can be further increased by post-processing.

The controlled assembly of individual CNTs reported here results directly from the interaction between the polarizable CNTs and the applied AC field. The proposed multi-step process is illustrated in Figure 3. When an AC field was applied, the polarized CNTs in water were first aligned along the field direction due to the torque acting upon the induced dipole (step 1, Fig. 3). This is a well documented phenomenon for polarizable particles and has recently been demonstrated for CNTs using a symmetric AC field. An estimate of the torque acting on an individual nanotube gives a value of 4 × 10⁻¹⁹ N m, which would generate an effective force on its ends that is about two orders of magnitude higher than the gravitational force acting on the tube. Under an asymmetric inhomogeneous field when the AC frequency and dielectric constant of the medium were carefully chosen, the aligned CNTs were driven by the field gradient towards the high field region near the W tip (step 2). The first group of CNTs adhered to the apex of the W tip and became the new outermost surface of the electrode where the next CNT precipitated. With continuous migration and precipitation of CNTs the structure grew along the field line towards the counter electrode (step 3). By gradually withdrawing the W electrode from the liquid such that only the tip of the CNT fibril was in contact with the liquid surface, precipitation and growth were confined within the liquid meniscus, which ensured that a fibril with a small and uniform diameter was formed (step 4). The alignment of the nanotubes in the fibrils, their high adhesion and the overall smoothness of the assemblies are likely to be strongly enhanced by the capillary pressure of the water in-
terface around the withdrawing fibril. An estimate of the capillary pressure acting on the surface of a water cylinder of such diameter gives a value ~ 720 kPa, more than enough to compress and align the fiber. In addition to that, capillary forces that are enormous on that length scale, estimated to be as high as $3 \times 10^{-5}$ N, can be generated by the water meniscus on misaligned nanotubes that protrude from the liquid surface.

Due to the difference in the polarizability of the different species, it may be possible to select the frequency of the AC field and the dielectric constant of the medium to achieve selective deposition. For example, it is principally possible to select the AC frequency such that the CNTs are preferentially attracted to the high field region while the impurity phases are left behind. We believe this may be the reason why the fibrils fabricated by this process are remarkably free of impurities.

There is no intrinsic limit on the length of the fibril that can be fabricated. At the low end, we showed sub-micrometer diameter fibrils with 2–3 μm in length. With better control of the suspension and the withdrawal rate, it is likely that a single CNT can also be deposited. The short fibrils (length < 50 μm) are relatively stiff. They have been used to obtain scanning tunneling microscope images of metal structures. Because of the small diameter and large aspect ratio, these tips can potentially increase the imaging depth of the instrument beyond what is afforded by the regular and single CNT tips. They are also stable electron field emitters. A stable emission current of 5 μA has been obtained from a single CNT fibril. At the high end, we have fabricated fibers over 1 cm in length. The long fibers are flexible and can bend sharply without fracture, demonstrating the strong van der Waals bonding between the aligned CNTs within the fiber.

The technique also enables parallel processing of many individual structures at the same time. To demonstrate this, two CNT fibrils were simultaneously assembled on two W tips using the same suspension. Figure 4 is an optical microscope image showing the two fibrils being drawn from the CNT–water suspension.

The dielectrophoresis process described here is versatile method for controlled assembly of individual nanostructures into functional forms. The method has several unique features and advantages. It affords fine control of the length and diameter of the fibril, potential for selective deposition, and the capability of parallel processing. Compared to the aligned CNT fibers made by DC electrophoretic deposition, fibrils assembled by the present method have much smaller diameters. By utilizing the asymmetric AC field to manipulate the polarizable CNTs, the fibrils are assembled without the use of chemical chargers which is important to preserve the intrinsic properties of the nanotubes. The technique can be used to fabricate CNT based SPM probes, electron field emitters, microelectrodes for electrochemical studies, and ultra-thin conducting fibers. The methodology can also be used to assemble fibrils using nanostructured building blocks other than the carbon nanotube demonstrated here.

Experimental

A schematic of the experimental set-up is shown in Figure 5, and is very similar to the system used by Rinzler and co-workers to make aligned CNT fibers by DC electrophoretic deposition. A W tip prepared by chemical etching was used as the working electrode and a small metal ring as the counter electrode. They were mounted on separate translation stages and were placed under an optical microscope. SWNTs were first purified, etched to ~2 μm in bundle length, and rendered hydrophilic. They were then dispersed in de-ionized water. A droplet of the nanotube suspension was placed inside the metal ring. To begin the deposition, an AC field (10 V at 2 MHz) was first applied between the two electrodes. The W electrode was translated horizontally to contact the CNT–water suspension and was gradually withdrawn under the electrical field until a fibril of the desired length was formed.

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Photo-Induced Orientation of a Film of Ladderlike Polysiloxane Bearing Dual Photoactive Side Groups**

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The control of the orientation of liquid crystalline molecules is essential in liquid crystal displays (LCDs), and is usually achieved by coating an alignment film on the conductive ITO (indium tin oxide) glass surface. The photo-alignment (PA) technique as one promising alternative to the widely used conventional rubbing process of a polyimide (PI) substrate has been studied extensively in the last decade, because it provides a simple and non-contact fabrication process suitable for advanced thin film transistor (TFT) LCDs. In principle, the PA materials can be primarily divided into two categories based on the type of functional groups employed. The first ones are capable of undergoing photo-induced isomerization from trans isomer (E-isomer) to cis-isomer (Z-isomer) and vice versa; this category includes molecules such as azobenzene-containing polymers.[1] The second category consists of polymers that can be anisotropically photo-cross-linked on illumination with linear polarized ultraviolet (LPUV) light; this includes examples such as polymers containing cinnamoyl or coumarin groups. In particular, Schadt[2b-d] and O’Neill and Kelly[4] recently demonstrated that the films based on coumarin exhibit high sensitivities and high pretilt angles (up to 7.5°), although the alignment was ascribed to unstable photo-degradation rather than cross-linking. However, despite the promising future of the PA technique, the search for materials possessing fine comprehensive performance still remains a great challenge.

As an inorganic–organic hybrid, the ladder-like polysiloxanes (LPSs) possess many excellent properties, such as being colorless and transparent, glasslike film-forming ability, high adhesion to glass and silicon chips, and superior solubility in common organic solvents, and are potentially ideal skeleton materials for PA applications. Accordingly, a novel LPS containing dual photo-reactive groups, cinnamoyl and 3-nitrobenzene, attached in a side-on fashion, was synthesized (Scheme 1, which also shows the structure of the final polymer). The molecular design was based on the following considerations:

- the azobenzene-containing polymer films often have a higher degree of tilted orientation and photosensitivity than the photo-cross-linking ones;[7]
- the threshold dose required to obtain a superior alignment for the side-on azo-grafted polymer is substantially smaller than that of the end-on ones;[8]
- both the photo-orientation and photo-cross-linking of the neighboring dual moieties would take place collaboratively after proper irradiation and most likely result in better alignment stability.

As expected, the LC cell assembled using the LPS-CA30 coated substrates exhibits a uniformly homogeneous alignment (almost mono-domain) with a long temporal stability (over one year at room temperature) and an adjustable tilt angle (θ = 1–7°) by variance in UV-light intensity (2–5 mW cm⁻²). The macroscopic orientation behavior of the LC cell was observed by polarizing optical microscopy (POM). It was noted that annealing after illumination markedly improved the alignment quality. A few silk-like defects on the dark-field image were self-healed after annealing or just leaving overnight, and the θ values increased by 2–3°.

In order to morphologically gain a deep insight into the mechanism of PA and the pretilt generation at the molecular level, the photo-induced dichroism difference (ΔA = A⊥−A∥) of the LPS-CA30-based PA film was examined by a polarized UV spectrometer. As shown in Figure 1, both the absorbance of the azobenzene group (λ_{max} = 375 nm) and of the cinnamoyl group (λ_{max} = 255 nm) show negative dichroism (ΔA < 0) simultaneously, implying that the photoreactions of the dual photo-reactive groups jointly participate in the generation of azimuthal anisotropy of the film; the in-plane absorbencies of both A⊥ and A∥ of the azobenzene group are reduced concurrently after irradiation, suggesting that the E–Z–E isomerization of the azobenzene groups leads primarily to an out-of-plane (spatial) reorientation. Remarkably, this PA film with dual photoreactive groups induces a homogeneous alignment

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