

Self-Assembly of Carbon Nanotubes**

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Self-assembly is an efficient and often preferred process to assemble micro- and nano- objects into ordered macroscopic structures.^[1] It has been utilized in recent years to produce functional materials such as photonic crystals,^[2] nanocomposites,^[3] and ordered DNA structures.^[4] Here we report self-assembly of pre-formed carbon nanotubes (CNTs) into hierarchical structures with controlled nanotube orientation. Patterned and periodic structures comprising CNTs can be readily assembled on glass and other suitable supporting surfaces at room temperature. The self-assembled nanotube solids exhibit optical and electrical anisotropy expected from the properties of their basic building blocks. With improved uniformity of the CNTs, the method can lead to three-dimensionally ordered structures and possibly single crystals of CNTs. This room temperature self-assembly method is advantageous for fabrication of certain devices such as CNT cathodes for field-emission displays. The method can be readily applied to other one-dimensional nanostructures.

The starting materials are single-walled carbon nanotube (SWNT) bundles synthesized by the laser ablation method and are purified by reflux in hydrogen peroxide and filtration.^[5] The average lengths of the purified SWNT bundles (typically $>10\text{ }\mu\text{m}$) were reduced to $\sim 2\text{ }\mu\text{m}$ and $\sim 0.5\text{ }\mu\text{m}$, by chemical etching using $\text{H}_2\text{SO}_4/\text{HNO}_3$.^[6,7] The processed samples were rinsed in deionized water and annealed at 200°C in 10^{-6} torr dynamic vacuum before use. As shown by the electron micrographs in Figure 1, the morphology of the SWNT bundles changed from that of highly entangled strands to rigid-rod-like after etching. The frequencies of the SWNT Raman-active modes are the same before and after etching.

The shortened SWNTs were dispersed in deionized water. In contrast to dispersions made with as-synthesized SWNT materials, a homogeneous suspension was stabilized up to 1.0 g L^{-1} without flocculation for several days. A clean hydrophilic glass slide was then immersed vertically into the SWNT/water suspension at room temperature, as illustrated in Figure 2. Initially no nanotubes transferred to the substrate.

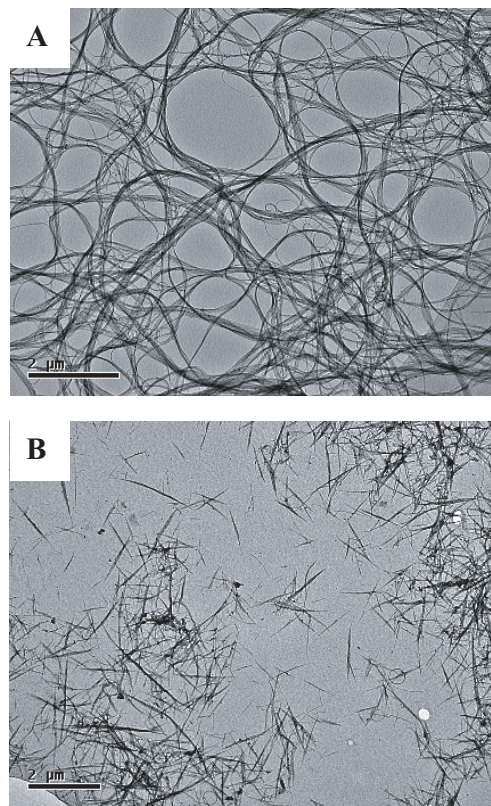


Fig. 1. Transmission electron micrographs of A) purified SWNTs and B) etched SWNTs with average bundle lengths of $2\text{ }\mu\text{m}$.

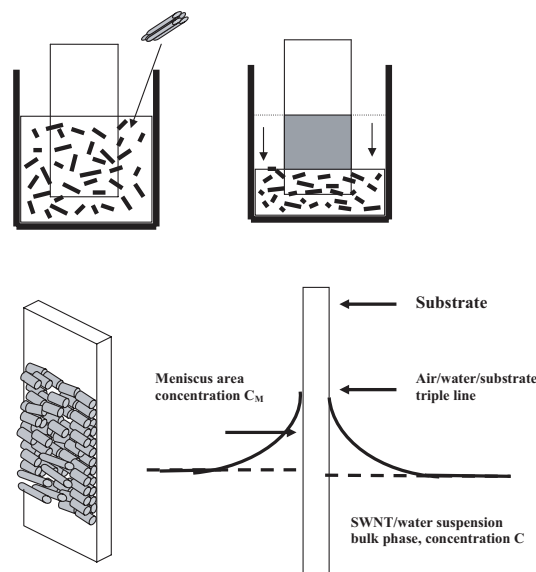


Fig. 2. A schematic illustration of the self-assembly process. Short SWNTs were dispersed in deionized water to form a stable suspension into which a hydrophilic glass slide was vertically immersed. With gradual evaporation of the water at room temperature, the SWNT bundles self-assembled on the glass substrate around the air/water/substrate triple line. As the triple line progressed downwards, a continuous SWNT film was formed on the substrate.

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When the water gradually evaporated the nanotubes were found to assemble on the glass surface. Further inspection showed that deposition occurred only along the air/liquid/substrate triple line; no nanotubes were found on the portion of

the substrate immersed in the suspension. As the triple line progressed downward, a continuous SWNT film formed.

Optical and scanning electron microscopy (SEM) measurements showed that the films have shiny surfaces and are uniform in thickness (Fig. 3). They have stepwise sharp edges that are straight at the substrate/film interface. The thickness of the films increased from less than 0.1 μm to over 1 μm with

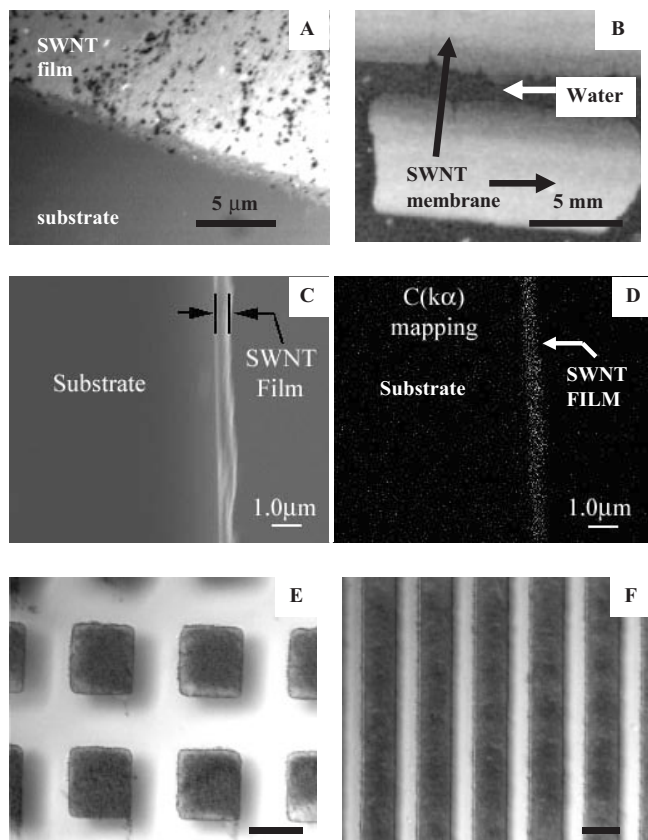


Fig. 3. A) An optical micrograph of a self-assembled SWNT film on a glass substrate. The dark spots are micropores on the film surface. B) Free-standing SWNT membranes floating on the water surface. C,D) An edge-on SEM secondary electron image (C) and EDS element C(K α) mapping (D) of a SWNT membrane on a Si substrate. As shown, the thickness of the membrane is about 0.5 μm . The SWNT film was precipitated from a 1 g L⁻¹ SWNT/water suspension. E,F) Patterned SWNT structures formed by the self-assembly process. Hydrophobic substrates were first patterned with periodic hydrophilic regions. SWNTs dispersed in water self-assembled on patterned hydrophilic regions. The squares (E) are 100 $\times$ 100 μm^2 and the stripes (F) are 100 μm in width. The shadows are due to reflections from the surface on which the samples (glass substrates) were placed. (The scales in (E) and (F) are 100 μm).

increasing nanotube concentration in the suspension. Thick films can be removed from the substrate by stirring in water and were often torn into smaller pieces ($\sim 5\times 10$ mm) of free-standing membranes that could float on the water surface (Fig. 3B). The membranes have regular geometry and sharp edges suggesting internal ordering.

When a hydrophobic substrate (a glass slide spin coated with a thin layer of polystyrene) was used, no carbon nanotubes deposited under otherwise identical conditions. This selectivity enabled the fabrication of patterned nanotube structures by controlling the functionality of the substrates. As

demonstrated in Figures 3E,F, periodic SWNT structures with a characteristic dimension of 100 μm were readily deposited on glass substrates with pre-patterned hydrophobic and hydrophilic regions. The well-defined CNT structures can be utilized as, for example, the basic field-emission pixels for field-emission displays. The efficient room-temperature deposition process is attractive compared to the high-temperature chemical vapor deposition process, especially for the low melting temperature glass substrates preferred for display applications.

Transmission electron microscopy (TEM) examinations of the free-standing membranes revealed that the SWNT bundles in these self-assembled structures were orientationally ordered (Fig. 4A). The longitudinal axes of the nanotubes lay on the substrate surface and were along the air/water/substrate triple line direction. The packing density of the nanotubes is substantially higher than that of the “nanotube papers” formed by filtration. As shown in the TEM image, the thin membrane was only a few bundles in thickness. Results from Fourier transformation of the real-space TEM image in-

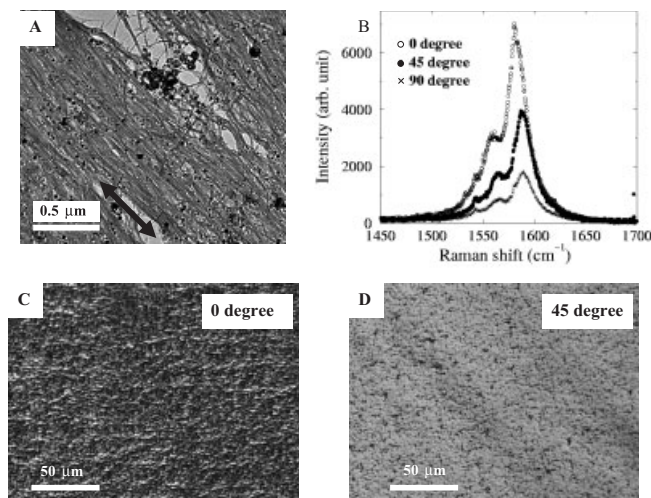


Fig. 4. A) TEM image of a self-assembled SWNT membrane comprising 0.5 μm length bundles. The membranes are only a few bundles thick and were partially torn when picked up by the TEM grid. The dark particles are the residual metal catalysts. The arrow indicates the triple line direction. B) Polarized Raman spectra from a self-assembled SWNT film measured using a micro-Raman spectrometer in the back-scattering geometry and VV configuration. The incident laser wavelength is 514 nm. C,D) Polarized optical microscope images of a thick self-assembled SWNT film (2 μm bundle length) taken using a white incident light and a pair of cross-polar polarizer and analyzer. The nanotube alignment direction was 0° (C) and 45° (D) with respect to the polarizer.

indicated that the SWNT bundles have a long-range orientational ordering but no translational ordering, similar to the structure of nematic liquid crystals. The degree of ordering depended on the aspect ratio of the nanotubes and the film thickness. Thin films of short nanotubes in general have a higher degree of ordering than thick films with long nanotubes. The longer bundles (2 μm length) formed a polycrystalline-type structure with well-ordered domains and partial alignment of neighboring domains.

Long-range ordering of the SWNTs in the macroscopic structures was confirmed by polarized Raman spectroscopy

studies. Figure 4B shows the SWNT tangential modes recorded using a micro-Raman spectrometer (DILOR XY) in back-scattering geometry and VV configuration (same polarization for the incident and scattered light). The polarized 514 nm incident laser was focused by a 10× microscope objective to 100 μm diameter spot size. The intensities of the SWNT tangential mode decreased with increasing sample rotation angle (at 0°, the laser polarization direction is parallel to the sample alignment direction). The angular dependence of the relative intensities of SWNT tangential modes measured from the macroscopic samples is similar to the published result obtained from a microscopic sample comprising a few aligned SWNT bundles,^[8,9] confirming that the self-assembled SWNT films are highly ordered.

Under a polarized optical microscope, the macroscopic SWNT films showed birefringence, with extinction at 0° (nanotube alignment direction parallel to the polarization direction) and 90° and maximum transparency at 45° over the entire surface area (Figs. 4C,D). The result is consistent with the expected anisotropic polarizability of the individual carbon nanotubes and demonstrates long-range orientational ordering of these materials. Preliminary transport measurements performed on thick films show that, similar to the results from the magnetically aligned nanotube ribbons,^[10] the electrical conductivity of the self-assembled SWNT film is substantially higher parallel than perpendicular to the alignment direction.

The hydrophilic nature of etched SWNT bundles is attributed to the presence of sidewall defects created by chemical etching. High-resolution TEM studies show that the surfaces of the SWNT bundles become rugged and are often coated with a thin layer of amorphous carbon after etching. Similar to the dangling bonds on the opened ends, these sidewall defects are likely to be terminated by polar groups that make the nanotube hydrophilic. The etched SWNTs can no longer be dispersed in water if vacuum annealed at temperatures above 400 °C, a condition known to “heal” the defects on the graphene shells.^[11] Our HRTEM measurements show that the clear and smooth lattice fringes of the SWNTs re-appeared after annealing at 400 °C in 10^{−6} torr vacuum, which is below the melting temperature of the glass substrate.

We propose that self-assembly of SWNTs on solid substrates is due to heterogeneous nucleation of nanotubes from a locally super-saturated suspension. When a hydrophilic substrate was immersed into a stable suspension with a nanotube concentration C_0 less than a critical concentration C^* , no deposition occurred initially although the suspension wetted the substrate (Fig. 2). With gradual evaporation of the water, the overall nanotube concentration increased. Under non-equilibrium conditions, the local nanotube concentration in the meniscus area, C_M , should be much higher than the overall concentration C . If the initial concentration C_0 is close to C^* and the evaporation rate is sufficiently high, C_M can exceed C^* , which results in precipitation of the CNTs from the suspension. The results reported here indicate that heterogeneous nucleation on hydrophilic surfaces is energetically more

favorable than homogeneous nucleation. If C_0 is substantially smaller than C^* , it is likely that $C_M < C^*$ even at a high evaporation rate, in which case no deposition of CNTs should occur. This is consistent with the experimental observation that no SWNTs transferred to the glass slide when $C_0 < 0.1 \text{ g L}^{-1}$. This mechanism is in essence the classic heterogeneous nucleation process^[12] and is similar to the one proposed for self-assembly of nanocomposites via selective solvent evaporation.^[3]

Similar to the case of nematic liquid crystals and Langmuir–Blodgett films, the driving force for ordering is attributed to maximizing the van der Waals interaction between the near-neighbor CNTs. The dimension of the etched SWNT bundles is in fact similar to some of the large virus molecules known to form liquid crystal phases. It is likely that alignment was also assisted by the surface tension at the interface between water and the hydrophilic substrate. Such forces are known to contribute to the alignment of large organic molecules such as DNA strands under similar conditions.^[4]

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Layer-by-Layer Assembly of Polythiophene

By Lei Zhai and Richard D. McCullough*

The high conductivity, stability, and processibility of head-to-tail polythiophene has stimulated a lot of interest in the utilization of this fascinating material as active electronic elements in various thin film devices and sensors.^[1,2] We have been interested in using a simple dipping method to facilitate

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