

Ring–Ribbon Transition and Parallel Alignment in SWNT Films on Polyelectrolytes

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A simple and reliable method of permanent organization of SWNTs into morphologically different films is described. Under standard adsorption conditions, SWNTs form films from randomly intersecting nanotubes. It was found that virtually perfect rings from single SWNTs also form spontaneously in these films. Adsorption in laminar flow produces SWNT ribbons with parallel alignment of the nanotubes. Further increase of the flow rate detaches SWNT from the surface.

The properties of carbon nanostructures and single wall carbon nanotubes (SWNTs) in particular provide a strong incentive for the design of new materials and nanoscale constructs. SWNTs combine high aspect ratio, small diameter, light weight, and high strength, which make them a rich platform for developing new nanostructured composites and advanced electronics.¹ The functionality of both classes of applications is directly dependent on the organization of SWNT at the nanoscale. Besides being of considerable fundamental importance, spontaneous and external stimuli-induced SWNT superstructures are expected to play a major role in future and emerging technologies and present a formidable challenge.

When applied to SWNT-reinforced composite materials, alignment of nanotubes is one of the most desirable qualities affecting conductivity, optical properties, and strength. Well-aligned SWNT imbedded in polymer matrix is the fundamental milestone for manufacturing of composites, which should exhibit record properties. Significant advances in this field have been achieved by using traditional methods of composite organization such as extrusion.² The layer-by-layer (LBL) assembly technique, a powerful methodology for making nanometer-scale composites based on omnipresent electrostatic and van der Waals interactions, recently demonstrated exceptional potential for fabrication of SWNT composites and tailored SWNT architectures.³ Unlike other methods of composite manufacturing, LBL allows an excellent degree of control over their organization, and one of the principal steps toward SWNT composites with controlled lateral orientation is demonstrated in this paper. Transversal organization of the multilayers leading to stratified composite films has been already obtained.⁴ It is

important to demonstrate the new level of organization: a degree of lateral ordering in each adsorption layer.

Here we demonstrate a simple and reliable method for permanently organizing SWNTs into morphologically different films (i.e., fibers and coils of preferentially oriented SWNT) taking advantage of the approaches used in SWNT electronics employing a laminar flow gradient.⁵ The parallel alignment of the nanotubes in SWNT films on polyelectrolyte surfaces necessary for the further development of nanotube-reinforced composites has been accomplished. Additionally, a spontaneous formation of rings in contact with polyelectrolyte films was observed, which is a remarkable process by itself considering the geometrical perfection of the obtained rings. Increase of the shear force of the laminar flow results in the ring opening and eventual formation of parallel SWNT strands packed in ribbons. Thus, both spontaneous and external stimuli-induced SWNT superstructures can be identified in one simple system.

SWNT–COOH dispersions in water were prepared as described elsewhere.^{3a,6} Their films were generated on Si wafers coated with a layer of polyethylene imine (PEI) obtained by immersion in solution of PEI in water for 60 min followed by drying in air.⁷ Multipoint electrostatic interactions guarantee the efficient association between the negatively charged carboxylic groups in SWNT–COOH and the positive charges of PEI leading to a film of intricately intertwined carbon nanotubes. van der Waals attractions between bundles of SWNTs are likely to be responsible for the entangling in areas, where low electrostatic repulsion is operative (i.e., low carboxylic acid coverage). Please note that the amount of oxidized flat graphite sheets or other forms of carbon colloids/metal impurities is very small.

In rarified films with lower SWNT coverage obtained for shorter adsorption times (30 min), both the geometry of individual SWNT in the LBL assemblies and the effects of deposition conditions on film morphology can be examined. As such, the presence of virtually perfect SWNT circles with a diameter of 100–500 nm often can be seen in the AFM images: see Figure 1. Previously the formation of rings was

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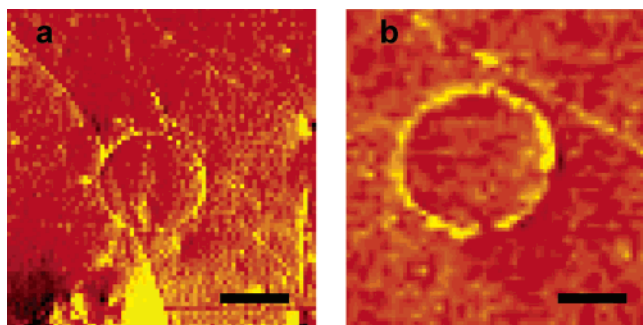


Figure 1. (a, b) Phase contrast AFM images of the carbon nanotube ring structures adsorbed to the polyelectrolyte monolayer (Si wafer substrate). The bars represent 350 nm (a) and 250 nm (b).

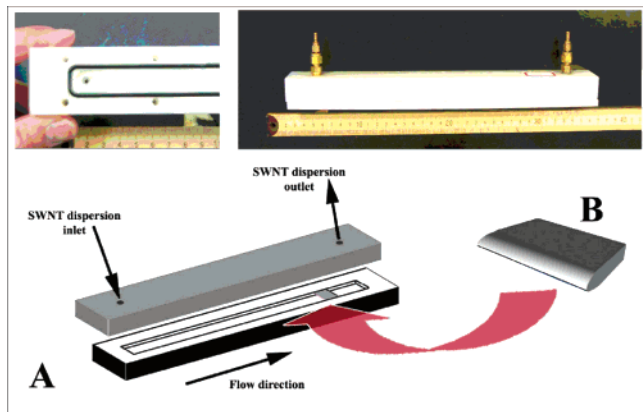


Figure 2. Schematic representation of the laminar flow cell.

seen only with head-to-tail chemically cross-linked systems.⁸ In the polyelectrolyte films, similar circular structures of SWNTs are likely to form due to van der Waals interaction-driven wrapping of the polyelectrolyte partially detached from the PEI adsorption layer (loops and ends). They form spontaneously during the attachment of SWNT to the polymer-modified surface.

Similarly to other processing techniques (i.e., extrusion and spin-casting) liquid flow conditions, applied during the SWNT deposition, significantly affect the morphology of the film. To investigate these effects, a special flow cell was constructed which provides laminar flow of liquid along the sample surface: a schematic representation is shown in Figure 2.

The stream of SWNT dispersion directed along the substrate was controlled to limit the Reynolds number, Re , below 2000. When the flow rate was 5 mL/min, $Re = 225$, one could see the gradual straightening of the nanotubes (Figure 3b). With further increase of the flow to 10 mL/min, $Re = 450$, one can see stretching of the nanotubes along the flow as shown in Figure 3c. No circular superstructures (vide infra) could be seen in the AFM images obtained in the flow cell, which indicates the reversible formation of the rings and their opening under the shear force. Interestingly, the lateral aligning of the tubes is also accompanied by the enhanced bundling in the surface plane. The width of these flat bundles or ribbons ranges from 30 to 80 nm, indicating that there are several dozens of individual SWNTs in them (Figure 3c). This effect is qualitatively similar to ribbon self-assembly observed by Vigolo et al.^{2a} Such morphology also maximizes the attraction to the plane and van der Waals forces between SWNTs. Many ribbons fork and then merge with each other depending on the local laminar flow conditions. The height of the ribbons does not exceed 2 nm, which is consistent with formation of 0.3–0.5 nm layer of polymer and SWNT. One should also notice that the overall

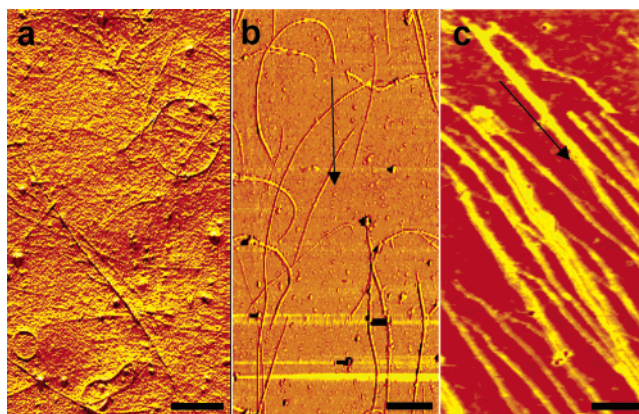


Figure 3. Phase contrast AFM images of carbon nanotubes layers adsorbed to the polyelectrolyte monolayer in static conditions (a) and under laminar flow (b, c). The bars represent 400 nm (a, b) and 300 nm (c), and the arrows indicate the direction of the laminar flow.

density of SWNT in the adsorbed layer reduces with the increase of the flow. Upon further increase of the flow (20 mL/min) the turbulence increases and the shear force detaches the nanotubes from the surface.

In conclusion, two types of SWNT organized structures have been observed in polyelectrolyte adsorption films: self-assembled SWNT rings and flow-induced parallel ribbons. The rings are likely to form directly on the surface of the polyelectrolyte-coated substrates because their substantial quantity would otherwise be observed in dense SWNT LBL films.^{3a} The actual mechanism of SWNT bending into a circle during electrostatic association with polyelectrolytes remains an open question. However, ring formation clearly indicates substantial mobility of the SWNT in the adsorption layer, which can also be seen in ring opening and has been utilized here for SWNT flow alignment. With respect to the ribbons, it is important to note that they represent the first step to highly organized LBL multilayer composites with a specific orientation of the nanotubes in each layer leading to materials with mechanical, optical, and electrical characteristics hard to achieve by other means including melt processing methods with polymers—poly(methyl methacrylate) etc.^{9,a,b}—or introduction of strong magnetic^{9c} or electric fields.^{9d}

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(6) SWNTs were manufactured by laser vaporization of carbon rods, which are doped with Co/Ni in a 1:1 ratio in an atmosphere of Ar.³ A suspension of SWNT raw material was refluxed in 65% HNO₃ and subsequently purified by centrifugation. Supplemented by sonication, this treatment results in the partial oxidation of ca. 5% of the total number of carbon atoms both in caps and in walls of SWNT. The presence of carboxylic acid groups affords metastable SWNT dispersions after 1 min sonication in deionized water without any additional surfactant.

(7) 1% solution of PEI, pH = 8.5; SWNT, pH = 6.8, rinsing bath; DI water for rinsing, pH = 8.5. All solutions were made in DI water. Wafers/glass slides were cleaned in piranha solution, rinsed with DI water, sonicated for 15 min, and again thoroughly rinsed with DI water. After that, they were coated with a precursor layer: PEI and PAA (pH = 3), followed by deposition of PEI/SWNT. Exposure times of 10 and 60 min were used for polyelectrolytes and SWNT baths, respectively.

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