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Unidirectional Alignment of Carbon Nanotube Aggregates Using Friction-transferred Polymeric Films

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Aggregates of single-walled carbon nanotubes (SWCNTs) were deposited unidirectionally on highly oriented PTFE film made by friction transfer. The friction-transferred PTFE film possesses many straight channels of various sizes running along the transfer direction. SWCNT aggregates were preferentially deposited parallel to the channels when SWCNTs in a form of dry powder were sprinkled, as confirmed by Raman microscopy and anisotropic electrical resistivity. Furthermore, the SWCNT film can be transferred to another substrate surface by simply stamping the SWCNT/PTFE film on it.

Single-walled carbon nanotubes (SWCNTs) have been studied extensively for their excellent electrical, thermal, and mechanical properties in the past decade. For instance, large current-carrying capability of metallic SWCNTs is attractive in polymer composites for producing optically transparent conductive films.[1–3] Semiconducting SWCNTs can be alternatives for silicon-based components in electronic devices. Most of these applications require high orientation or precise positioning of individual SWCNT at nanometer scales. Yet, the characteristic string-like shape of SWCNT, with diameters on the order of a few nm and lengths up to a few µm, has posed a serious problem.[4] Additionally, the string-like shape implies that SWCNTs entangle easily. It is common to find SWCNTs as entangled aggregates if macroscopic amounts are gathered. Thus, for practical applications, it is important to develop a method to control orientation of each aggregate, in addition to a challenging task at an individual tube level. So far, the methods involving bundling,[5] electrospinning,[6] liquid crystals,[7] and shear flow[8] have been reported to align SWCNT aggregates. In order to be practical, however, the method must be simple, require a small number of processes, and be independent of the materials to which SWCNTs are fixed. In this study, we utilize an unidirectionally aligned polymer film made by friction transfer to orient the SWCNT aggregates. Moreover, the aligned SWCNT aggregates are transferred to other substrates by simply stamping the SWCNT/polymer film onto their surfaces.

Friction transfer has been applied to unidirectionally align polymers.[9] A solid crystalline polymer is rubbed against a substrate surface, the temperature of which is kept at just below the melting temperature of the polymer. The friction between the polymer and the substrate surface melts a small portion of the polymer. The melted polymer is transferred onto the substrate surface and crystallizes immediately to form a thin film with unidirectionally oriented molecules.[10,11] The polymers reported to be aligned by this method include Teflon [poly(tetrafluoroethylene) (PTFE)],[9] polysilane,[12] polythiophene,[13] polyfluorene (PFO),[14] poly(phenylenevinylene),[15] polystyrene,[16] and polyaniline.[17] Additionally, the film surface has many straight channels running along the rubbing direction, with depths ranging from nanometers to sub-millimeters. This wide range of channel sizes has allowed various materials with different sizes, from inorganic compounds to polymers,[9,18–22] to crystallize with crystalline axes aligned along the rubbing direction. Since as-grown SWCNT samples usually contain individually separated tubes as well as aggregates of different sizes, the friction-transferred polymeric film offers a possibility of accommodating various forms of SWCNT aggregates.

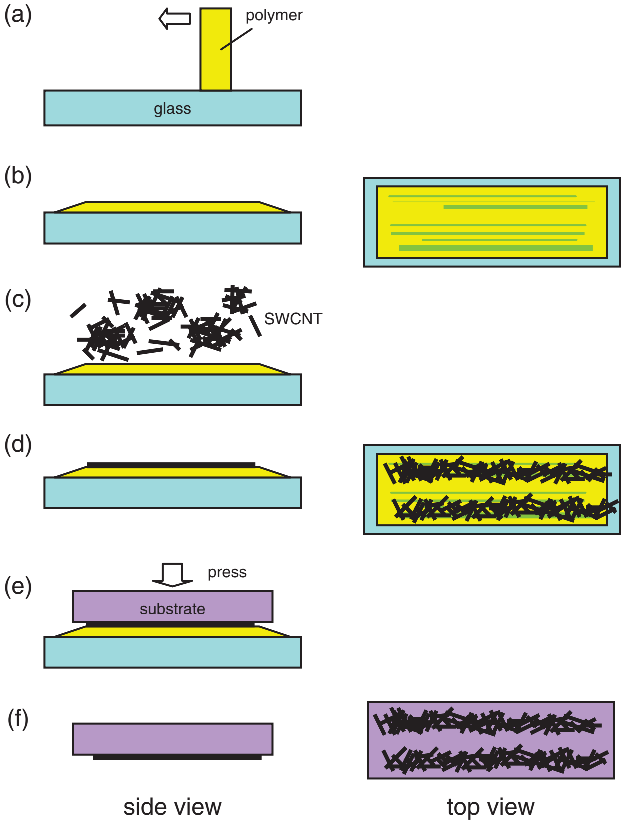

Figure 1. Aligning and transferring processes. (a) A solid PTFE block is rubbed against a heated glass to give a friction-transferred film (b). (c) Dry SWCNT powder is sprinkled on the PTFE film. (d) Removing the excess SWCNTs leaves aggregates aligned along the rubbing direction. (e) Pressing the 2nd substrate and (f) lifting off transfer the SWCNT aggregates onto the 2nd substrate.

We have tried several methods of deposition, such as casting SWCNT solutions or pressing a mass. The best result was obtained by using airborne SWCNTs. Figure 1 illustrates a typical aligning procedure. A Teflon block is rubbed against a heated glass (a) to form a friction-transferred PTFE film with many channels (b).[9] As-grown dry SWCNT (HiPco) powder is

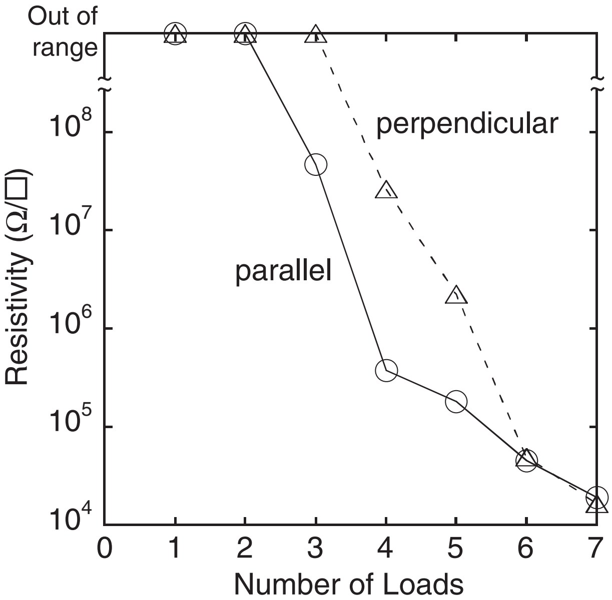

Figure 2. Surface electrical resistivities parallel and perpendicular to the rubbing direction, as measured by a four-probe method (Loresta-GP, Mitsubishi). A single load corresponds to one sprinkling and removing cycle.

blown up in the air and scattered over (or sprinkled) the Teflon film (c), and excess SWCNTs are removed gently by scraping or blowing air to leave only adhered aggregates (d). The processes (c) and (d) are repeated a number of times to study the effect of increasing deposited amounts.

Anisotropy of the resulting film is revealed by the electrical resistivities measured parallel and perpendicular to the rubbing direction when successively additional SWCNTs are loaded. In the case of the result shown in Figure 2, the first two loadings are not enough to develop SWCNT networks. At the 3rd loading, percolation occurs in the direction parallel to the rubbing direction whereas the network is still undeveloped in the perpendicular direction. The resistivity at the 4th loading is similar to a SWCNT film on glass made by layer-by-layer adsorption.[23] The anisotropy disappears when an excess amount of SWCNTs is deposited at the 6th loading, as evidenced by the fact that the resistivities of both directions merge to the value of excess SWCNTs deposited on an isotropic PTFE surface. Although the precise number of loads necessary to achieve percolation depended on the experiment, percolation in the parallel direction reproducibly appeared at the smaller number of loading than the perpendicular direction.

The distribution of SWCNTs on a polymer film is analyzed by Raman microscopy. The microscope acquires Raman spectrum at each point on the sample surface while scanning over the surface. As shown in Figure 3, SWCNTs exhibit a strong peak around 1580 cm^{-1}, where PTFE and glass have none. Plotting the intensity of this peak at each point on the surface results in a map showing the location of SWCNTs. Figure 4a reveals that the SWCNTs are distributed as thin bands having widths on the order of a few tens of μm aligned in the rubbing direction (the horizontal direction in this image), which can be contrasted with the random distribution on an isotropic film (Figure 4b). Scanning electron microscopy indicates that each band consists of heavily entangled SWCNT bundles (Figure 4c). Because these bundles are seen in the original SWCNT powder, the present deposition process is to link already aggregated SWCNTs along the channel.

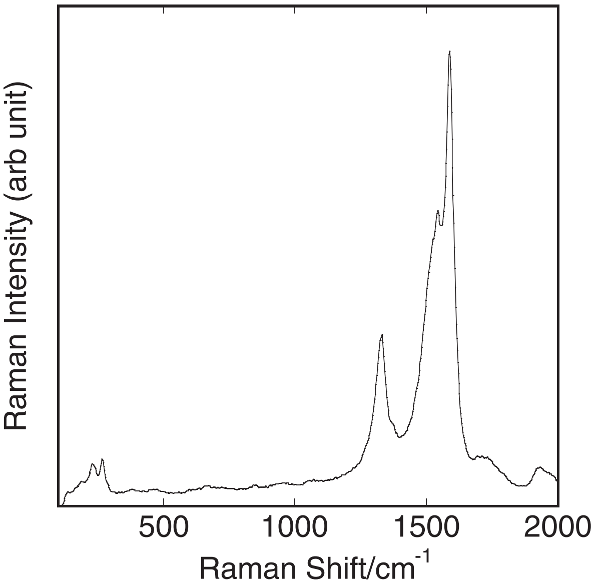

Figure 3. Raman spectrum of SWCNT on the friction-transferred PTFE film, probed by a 532-nm laser.

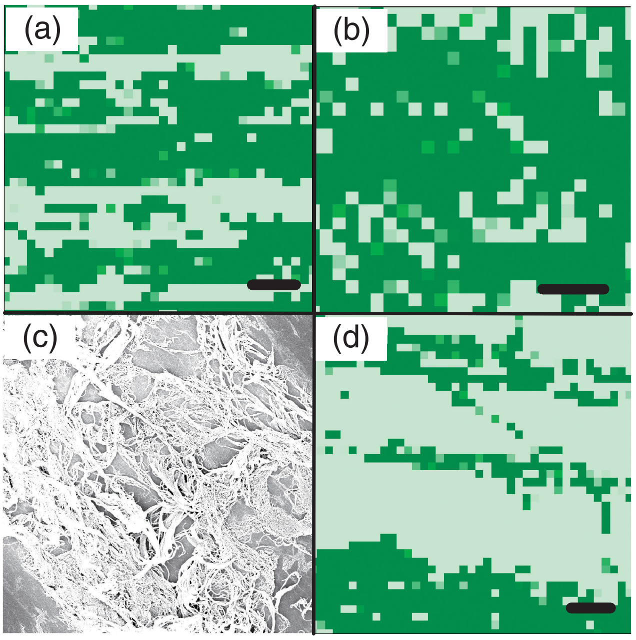

Figure 4. Raman mapping of SWCNTs on (a) a friction-transferred PTFE film and (b) an isotropic PTFE film. A darker area corresponds to a higher Raman intensity. The rubbing direction in (a) is horizontal. (c) SEM image of a deposited area in (a). (d) Raman mapping of SWCNTs on the silicon rubber transferred from the SWCNT/PTFE film. The scale bar is 10 μm.

The advantage of using PTFE is that the SWCNTs are only weakly adhered. Simply pressing the second substrate against the SWCNT/PTFE surface, as illustrated in Figure 1e as a "SWCNT stamping" step, transfers the SWCNTs onto the second surface. Figure 4d is an Raman map of SWCNTs on silicon rubber transferred by the SWCNT/PTFE stamping. The unidirectional alignment as determined by the rubbing direction in the original PTFE film is preserved. Although not all SWCNTs on the PTFE film have been transferred, it is enough to give the SWCNT/silicon rubber the same electrical resistivity as the original SWCNT/PTFE stamp.

In conclusion, we have demonstrated that sprinkling dry SWCNT powder on a friction-transferred polymeric film aligns the SWCNT aggregates in the rubbing direction. This is a simple method that requires only a few steps. Furthermore, the resulting SWCNT/PTFE film can be used as a stamp to transfer the aligned SWCNT aggregates to other substrates. Because the friction-transferred film has channels with various sizes down to molecular levels, the present method may be extended to align individually separated SWCNTs.

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