Large Area, Directionally Aligned Single-Walled Carbon Nanotube Films by Self-assembly and Compressed Sliding Methods

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ABSTRACT

We demonstrate the fabrication of well-aligned array of surface modified single-walled carbon nanotubes (SWNTs) and nano silver decorated SWNTs from their surfactant stabilized dispersions by self-assembly on solid substrates in a large area. The shape, rigidity and surface charge of the nanomaterials are found to be the key factors determining the alignment by self-assembly. We also demonstrate preparation of highly transparent conductive thin films (800±50 Ω/□, 95-97 %T at 550 nm) of directionally aligned SWNTs from high concentration aqueous dispersion of SWNT by compressed sliding of a thin liquid film between two glass plates. Evaluation of thin films by SEM, AFM, optical and electrical characterization demonstrates that SWNTs are directionally aligned with high density. Thin films of directionally aligned SWNTs can be used for photovoltaic and other optoelectronic application such as in touch screens, antistatic coatings, flat panel displays, optical communication devices, and solar cells.

Keywords: Carbon nanotube, Surface modification, Self-assembly, Sliding, Alignment.

1 INTRODUCTION

Carbon nanotubes (CNTs) and nano crystals are among the most promising materials predicted to impact future nanotechnology owing to their unique structural and electronic properties [1, 2]. Single-walled carbon nanotubes (SWNTs) have drawn great interests for application in a wide range of potential nano-devices owing to their exceptional mechanical, electrical, optical and thermal properties [3]. Functionalization of CNTs with various chemical groups and nanocrystals can further enhance the properties of CNTs. Alignment of CNTs from as produced materials is an important challenge for achieving novel or enhanced physical properties. Aligned assembly of carbon nanotube arrays have shown excellent electrical, opto-electronic and electromechanical properties compared to that of disordered network film [4]. Therefore, most of the realistic applications of SWNTs would require directional alignment of nanotubes as thin films or patterns on a substrate to explore their unique out standing properties.

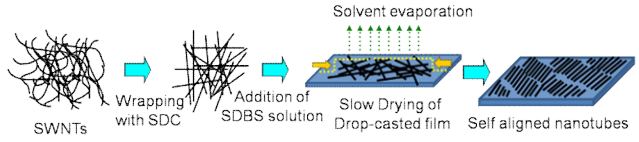
There are several different methods available for the alignment by pre or post synthesize processing of CNTs including chemical vapor deposition (CVD), dielectrophoresis, drawing polymer–CNT composite film, drop drying CNT film, Langmuir–Blodgett deposition, application of magnetic fields and electrospinning [5,6]. Large area crack alignments have been obtained from CNT aqueous dispersions by self organization of the surfactants on drying or due to the cracking mechanism in case of composites with polymer [7,8]. Recently, Liu et al. reported transfer and aligned assembly of large area CVD grown CNT films from growth substrates to receiver substrate by contact transfer and sliding [9]. In this contribution, we present two simple methods for the aligned assembly of SWNTs via self assembly of surface modified SWNTs and compressed sliding a thin liquid film of high concentration aqueous surfactant dispersion between two flat substrates. Surface modification of SWNTs by sodiumdeoxycholate (SDC), a bile acid salt with large and rigid hydrophobic moiety of a steroid skeleton, rendered a rigid shape and the further treatment with anionic surfactant sodiumdodecylbenzene sulfonate (SDBS) provided negatively charged surface. The self assembly of SWNTs and SWNT-Ag hybrid are driven by the shape, rigidity and surface charge. Compressed sliding of the SWNT liquid film between parallel surfaces causes mechanical stretching of the film, which lead to the formation of ultrathin film with directional orientation of nanotubes. The directionally oriented nanotube thin films can be used for applications such as chemical-gas sensor, bio sensors, catalysts, flexible displays, touch screens and solar cells.

2 EXPERIMENTAL

2.1 Self-assembly of Surface Modified SWNTs

An aqueous dispersion of CNT was prepared by ultra-sonic agitation of 20 mg SWNT (arc discharge, Iljin Nanotech Co., Korea) in 50 mL of 1 wt% SDC (Aldrich) solution. The dispersion was centrifuged at 6000 rpm for 30 min to remove larger bundles and impurities. To reduce the surface tension and also to generate negative charge on SWNTs, the dispersion was mixed with 0.1 wt% aqueous solution of SDBS in the ratio 1:2 or 1:4 (v/v). Thin films were prepared on cleaned glass and silicon substrates by spin coating, dip coating and drop deposition methods. A

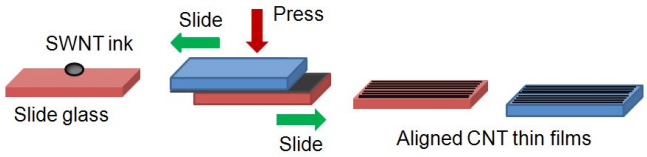
schematic illustration for self assembly in drop dried film of SWNT-SDC/SDBS is shown below.



Scheme 1. Fabrication of self assembled CNT array by drop drying

2.2 Directional Alignment of SWNTs by Sliding Method

High concentration SWNT ink was prepared by sonic agitation of 25 mg SWNTs immersed in 20 mL of 0.08% SDBS aqueous solution by high power ultrasound sonication for 15 min. The dispersion was then centrifuged at 6000 rpm for 30 min to remove larger bundles and impurities. The concentration of SWNT ink was ~1mg/mL. To prepare ultrathin aligned transparent films, 50 µL ink was placed at the center of a cleaned glass substrate and placed another substrate over it and pressed gently. Excess CNT ink was wiped off from the sides of substrate and, then it was slided one over the other at constant speed with pressing. The films were allowed to dry at room temperature under atmospheric conditions. A schematic illustration for the film fabrication by sliding method is depicted below. For annealing, the films were heated in hot air oven at 90 °C for 1h.



Scheme 2. Fabrication of directionally aligned thin film of SWNT by compressed sliding.

3 RESULTS AND DISCUSSION

3.1 Characterization and Evaluation of Aligned SWNT Films Prepared by Self-assembly of Surface Modified CNTs.

Scanning electron microscopic (SEM) images of SWNT thin films deposited on Si substrate is shown in Figure 1. The SEM image of SDC modified SWNTs (Fig. 1(a)) illustrates that the nanotubes are well dispersed and possess a rigid rod like structure. The large and rigid hydrophobic moiety of a steroid skeleton in the SDC molecule imparts rod-like rigid shape to originally flexible nanotubes [10]. Figure 1(b) and (c) show SEM images of aligned SWNT thin films prepared by drop drying from SWNT-SDC dispersion mixed SDBS solution in the ratio 1:2 and 1:4, respectively. The film with SWNT-SDC: SDBS in the ratio of 1:4 demonstrated high degree of alignment as well as high packing density compared to that of film with 1:2 ratios. Figure 1(d) displays densely aligned assembly of SWNT-Ag hybrid dispersed in SDBS solution. The self assembly of nanomaterials from surfactant dispersion is based on their shape, aspect ratio, surface charge and capillary action during the drying process [11]. The surface modification of SWNTs with SDC rendered a rigid shape and the subsequent treatment with anionic surfactant provided negatively charged surfaces. Similarly, decoration of SWNT surface with metal nanoparticles gave more rigid shape and the surfactant adsorbed on the surface provided a charged surface. Additionally, the surfactant helps uniform spreading of nanotubes by lowering surface tension and also reduces rupture of film by dewetting. The thin films of SWNT-SDC/SDBS (ratio, 1:4) prepared by spin coating and dip coating also demonstrated aligned assembly of nanotube (Fig. 1(e) and (f)), but the degree of alignment and packing density were relatively low compared to drop deposited films.

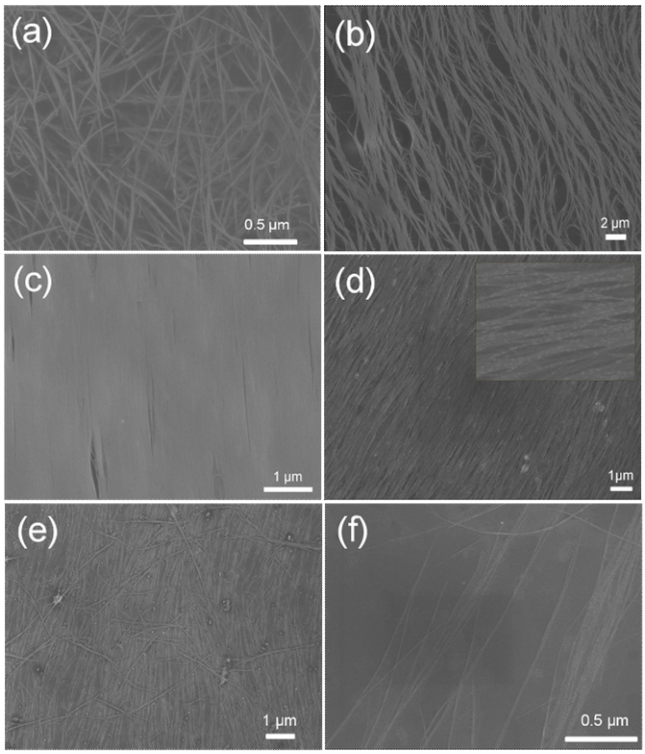


Figure 1. SEM images of (a) SWNT-SDC (b) SWNT-SDC/SDBS (ratio 1:2) (c) SWNT-SDC/SDBS (ratio 1:4) and (d) SWNT-Ag hybrid/SDBS thin films prepared by drop deposition. (e) & (f) thin film of SWNT-SDC/SDBS (ratio 1:4) prepared by dip coating and spin coating methods, respectively. Inset of Fig.1 (d) shows Ag nano particles decorated on SWNT surface.

Polarized spectroscopic techniques, including polarized Raman spectroscopy and / or polarized absorption spectroscopy have been shown to useful techniques for alignment characterization due to the strong anisotropic absorption of polarized radiation by SWNTs [12]. The optical absorption spectra of the sample films were measured at different rotation angles from -90 to 90 degree and the order of alignment was investigated as a function of wavelength. The intensity absorbance peak corresponding to S_{11} transition showed noticeable change with rotation angle. Figure 2 illustrates the angular dependence of absolute absorption for thin films corresponding to S_{11} transition at a wavelength of 1010 nm. The remarkable change in intensity of absorption band with rotation angle provides spectroscopic evidence for the directional alignment of the nanotubes.

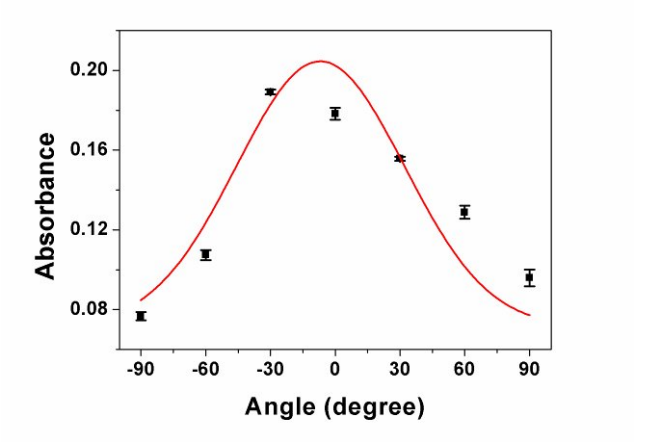


Figure 2. Angular dependence of S_{11} absorption peaks of aligned SWNT film

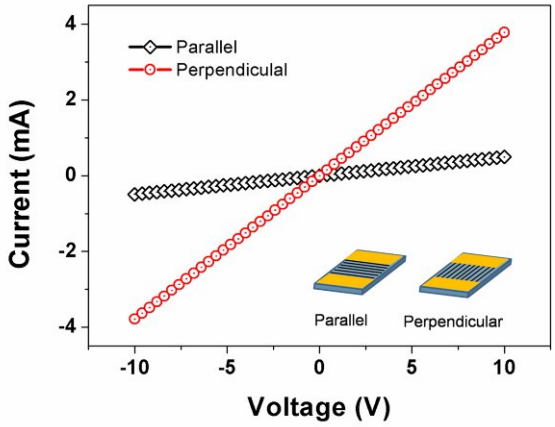
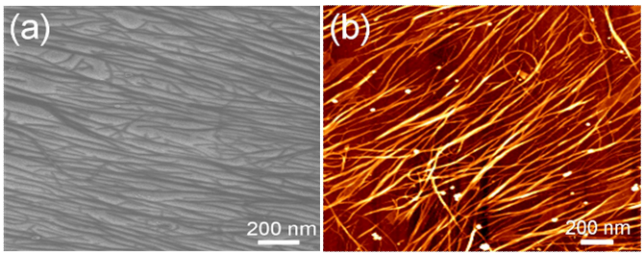


Figure 3. Current-voltage characteristic of SWNT film in which CNTs are aligned parallel and perpendicular to the electrodes.

Figure 3 shows the I-V characteristics of SWNT film corresponding to the electric field applied parallel and perpendicular to the SWNT alignment direction measured by depositing Au electrodes at 1 cm apart. The current was very low for parallel oriented nanotubes compared with that of CNTs oriented perpendicular direction against the electrodes. It implies to macroscopic anisotropic electrical transport in aligned nanotube films. Briefly, these results illustrate high order directional alignment and anisotropic behavior of self assembled nanotube arrays.

3.2 Characterization and Evaluation of Aligned SWNT Films Prepared by Sliding method

The SEM and AFM images in Figure 4 show that the nanotubes are horizontally aligned in the plane of the substrate by sliding the CNT liquid film in between two parallel substrates. The CNTs are in direct contact with each other though their ends, which make the easy transport of charge carriers along the aligned SWNT direction. The thickness of film measured by AFM line profile was 10±2 nm, which corresponds to the bundle diameter, illustrates the formation of monolayer SWNT array.



Figue 4. a) SEM and b) AFM images of horizontally aligned SWNT thin films prepared by sliding CNT liquid film between two glass slides.

When an external pressure is applied in perpendicular direction on sample ink drop placed in between two parallel flat substrates, a thin liquid film of nanotubes with monolayer thickness was formed owing to the reduction of gap between the parallel walls to minimum possible spacing. The mechanical stress exerted on the nanotube liquid film at such a small gap would be very huge and which make the original random network nanotubes in the film to orient in different directions. A one-dimensional flow of solution is developed when a pair of substrates is moved one over the other in opposite direction with uniform velocity under constant stress, which is believed to facilitate the aligned architecture nanotubes along the direction of sliding [13]. It is quite similar to mechanical stretching of solid SWNT film.

The surfactant molecule has a crucial role in this process to form uniform aligned SWNT film because it helps uniform spreading of nanotubes by lowering surface tension and also renders them to adhere firmly on the substrates. Experiments with surfactant free CNT dispersions failed to form uniform aligned film due to poor adhesion on the substrate and dewetting of the liquid film. To overcome the

issue of film rupture, the dewetting velocity (V_{dewet}) must be low so that the liquid film can dry before deformation of the film occurred by dewetting. The dewetting can be effectively avoided if drying time of liquid film is much shorter than the dewetting time, $t_{dewet} = L/V_{dewet,}$ where L is the characteristic length scale of the film [14]. Consequently, the dewetting can be minimized by lowering surface tension and by properly reducing the drying time of coated film. The surfactant SDBS satisfies these conditions. Since the thickness of film was nearly 10 nm, it quickly dried under atmospheric conditions.

Figure 5 shows angular dependence of optical absorption corresponding to S_{11} transition. The anisotropic optical absorption property demonstrates directional alignment of nanotubes in the plane of the substrate.

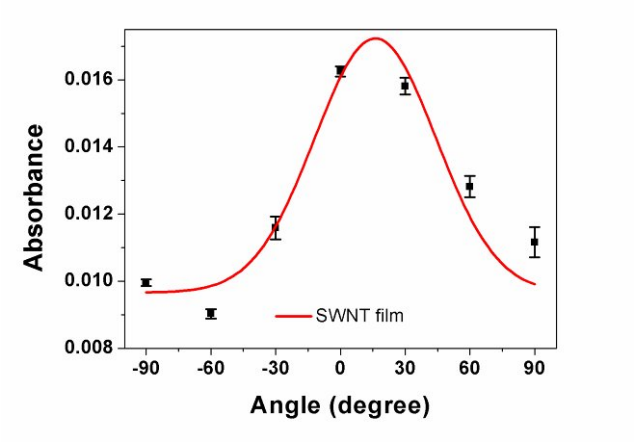


Figure 5. Angular dependence of S_{11} absorption peaks of aligned SWNT film

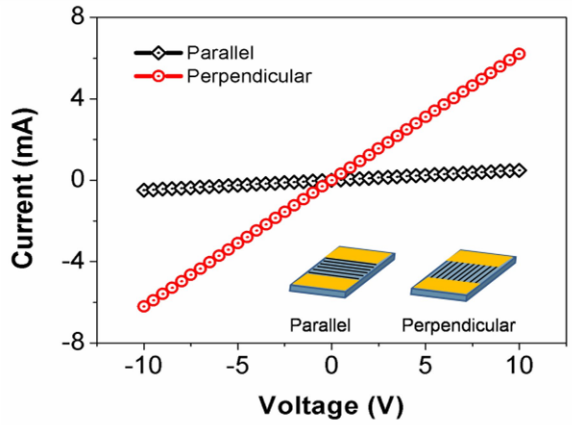


Figure 6. Current-voltage characteristic of SWNT film in which CNTs are aligned parallel and perpendicular to the electrodes.

The current-voltage characteristic of film in parallel and perpendicular directions of nanotube alignment direction (Fig.6) further illustrated directional orientation of nanotubes in the film prepared by sliding method. The ratio of resistivity for parallel ($R_{\parallel}$) to perpendicular ($R_{\perp}$) direction of SWNT film is 12.6, which shows the electrical anisotropic property. The number of inter-tube junctions in aligned nanotube film is very less compared to that in network film. Thin films prepared on glass substrate by sliding method demonstrated 95-97%T at 550 nm and sheet resistance of 800±50 Ω/□.

4 SUMMARY

In summary, we have fabricated large area directionally aligned thin films of CNTs by two simple methods. First, self assembled aligned array of surface modified SWNTs was fabricated by drop drying, spin coating and dip coating methods. We attribute that the rigidity of the nanostructure and surface charge are crucial factors for the alignment of SWNTs by self assembly. Second, compressed sliding of SWNT film between parallel substrates provided ultra-thin transparent conductive films with high degree of alignment of CNTs in the plane of the substrate. Directionally aligned monolayer of SWNTs can be used for transparent conductors, touch panel, field emission display applications.

5 REFERENCES

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