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The fabrication of single-walled carbon nanotube/polyelectrolyte multilayer composites by layer-by-layer assembly and magnetic field assisted alignment

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Abstract

Single-walled carbon nanotube (SWNT)/polymer composites are widely studied because of their potential for high mechanical performance and multifunctional applications. In order to realize highly ordered multilayer nanostructures, we combined the layer-by-layer (LBL) assembly method with magnetic force-induced alignment to fabricate SWNT/poly(ethylamine) (PEI) multilayer composites. The SWNTs were functionalized with the anionic surfactant sodium dodecylbenzenesulfonate (NaDDBS) to realize negative charge at pH > 7, while the PEI is positively charged at pH < 7. The LBL method is based on the electrostatic absorption between the charged SWNTs and PEI resin to form multilayer composites on a solid substrate polydimethylsiloxane. Since the fabricated thickness of each SWNT-NaDDBS/PEI bilayer is uniform (\sim 150 nm), the multilayer film thickness can be strictly controlled via the number of deposition cycles. A high magnetic field (8.5 Tesla) was used to align the SWNTs during the LBL process. The resultant LBL composite samples demonstrated high SWNT loading of approximately 50 wt% and uniform distribution of SWNTs in the multilayer structures, which was verified using a quartz crystal microbalance. Good alignment was also realized and observed through using high magnetic fields to align the nanotubes during the LBL deposition process. The results indicate that the LBL/magnetic alignment approach has potential for fabricating nanotube composites with highly ordered nanostructures for multifunctional materials and device applications.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs) have attracted considerable interests for use in fabricating composite materials [1–5]. SWNT is one of the most promising materials for developing new thin film materials and composites, including those for catalytic membranes, actuators, sensor devices and multifunctional composites applications [6–8]. SWNTs

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exhibit remarkable properties, such as extraordinary tensile strength and thermal and electrical conductivity in the direction along the tube axis. They are highly anisotropic nanoparticles with extremely large aspect ratios. Reports conclude that SWNT-reinforced polymer composites can realize significant improvement in mechanical properties and thermal and electrical properties at various SWNT loading levels [9–11]. Shear forces have been frequently used for aligning such nanoscale inclusions along the flow direction to reinforce mechanical properties. Well-aligned 10 wt% SWNT/PBO (poly(p-phenylene benzobisoxazole)) composite fiber exhibited electrically insulating behavior, while achieving significant mechanical improvement along the fiber direction [12, 13]. Several other methods were also used for SWNT alignment, such as electrical fields [14, 15], magnetic fields [16, 17], blown bubble [18, 19], spinning [20], mechanical stretching [21], melt extrusion [22] and slicing [23]. The advantages of using magnetic fields are that it not only can effectively induce SWNT alignment to develop bulk materials due to excellent magnetic field penetration capability, but it is also possible to control the orientation direction of carbon nanotubes (CNTs) with respect to the in-plane or film surface with coupling with LBL approach. Furthermore, aligned SWNT films of any desired nanotube orientation angles or angle combinations can be produced using this LBL and magnetic alignment process. The alignment direction of CNTs is according to the magnetic field direction in this process. By simply changing the substrate alignment to the magnetic field direction, it is possible to obtain any CNT alignment angles in a multilayer film deposited on a substrate. In this paper, the magnetic field is along vertical direction, and we only tested one CNT alignment angle which is also along the vertical direction to approve the concept.

Among the known nanomanufacturing methods, the layerby-layer assembly method is one of the most versatile techniques for fabricating multilayer composite films. Decher et al first introduced this method [24, 25] for fabricating multilayer complex films on planar substrates through the alternative deposition of oppositely charged polyelectrolytes in aqueous solutions. This technique was also applied by several groups by coating various particle surfaces and in constructing microcapsules [26–28]. Furthermore, non-charged driving forces, such as hydrogen bonds [29], covalent bond [30] and ligand bonds [31] were also used to fabricate multilayer complex films, which further broaden the LBL assembly technique [32, 33]. The SWNT content in a typical SWNT composite prepared by conventional melt mixing and extrusion is usually at a range of 0.5-15 wt% due to viscosity limitation, while the LBL assembly technique resulted in a nanotube content in the range as high as 50 wt% [34], which is much higher than other manufacturing methods.

This paper reports on a combined magnetic field alignment and LBL assembly to fabricate SWNTs/polymer multilayer composites with high nanotube loading and highly ordered structures. Water soluble dispersion of SWNTs was a key factor in our experiments. **SWNTs** are known to easily aggregate in most solvents because of the intense van der Waals interactions among the tubes due to large surface area of nanotubes. Such a limitation, which has presented great difficulties in SWNT manipulation, could be overcome through the surfactant functionalization of SWNTs [35, 36]. Researchers found that SWNTs were well-dispersed in the aqueous solution using surfactant sodium dodecylbenzenesulfonate (NaDDBS) during sonication dispersion [35]. Such SWNT-NaDDBS was negatively charged at pH < 7. The polymer used in the experiment was poly(ethyleneimine) (PEI), which is positively charged in an aqueous solution when pH > 7. Hence electrostatic absorption mechanism can be used to fabricate LBL SWNT composites. The SWNT/PEI LBL composites produced in this study were assembled onto a glass slide supported by alternating dipping of a solid polydimethylsiloxane (PDMS) substrate into a dispersed negative SWNT aqueous solution and a positive PEI aqueous solution.

Researchers have conducted calculations and experiential studies to illustrate the effectiveness of magnetic alignment of CNTs, revealing that significant alignment of SWNTs can be achieved when the magnetic field strength is more than 5 T [37–39]. Certainly, the higher magnetic field strength will lead to better CNT alignment. In this study, we used 8.5 T magnetic field for the alignment, which is available for us at the National High Magnetic Field Laboratory (NHMFL). Figure 1 shows the procedure of our LBL and magnetic alignment process. Based on the electrostatic absorption between the SWNT–NaDDBS and PEI, a multilayer of aligned SWNT–NaDDBS and FEI polymer layers were assembled on the substrate with well-controlled nanostructures.

2. Experimental details

2.1. Materials

SWNTs were purchased from Thomas Swan Co. Ltd. Branched polyethyleneimine (PEI, 50% aqueous solution) and polydimethylsiloxane (PDMS) were obtained from Aldrich and used as received. Sodium hydroxide and hydrochloric acid for pH adjustment were obtained from Aldrich. Deionized (DI) water was used in all solutions and rinsing procedures.

2.2. Preparation of [SWNT–NaDDBS/PEI]n LBL multilayer composites

The LBL assembly method was used to fabricate [SWNT-NaDDBS/PEI]n multilayer composites following guidance provided in [40]. The dispersed SWNT-NaDDBS aqueous solution was placed into a magnetic field for nanotube alignment. Briefly, 0.1 mg ml⁻¹ SWNTs were dispersed into an aqueous solution of 0.5% NaDDBS. The concentration was greater than the critical micellar concentration. The resulting dispersion was sonicated for 1 hour to provide a homogeneous black suspension. The dispersed SWNT solution was filtered by a nylon filter membrane with a pore size of 0.45 μ m. The resultant SWNT-covered membrane film was immersed in DI water and sonicated for 30 min. The SWNTs' concentration was approximately 0.2 mg ml⁻¹. Extra NaDDBS in the aqueous solution was removed, and the dispersed SWNTs-NaDDBS could be maintained as a stable aqueous solution for several weeks. The 0.5% PEI solution was at pH = 8.5, and the SWNT solution was at pH = 6.5. The beaker containing the SWNT-NaDDBS solution was placed in a magnetic field of 8.5 T.

The layer-by-layer assembly technique is a simple and common method used to fabricate thin films of nanoparticles and polyelectrolytes on solid substrates, such as glass slides or silicon wafers. PDMS was used as a solid substrate for the LBL assembling of the multilayer films in this study. Here,



Figure 1. Layer-by-layer assembled aligned SWNT multilayer composites with positively charged PEI and negatively charged SWNTs.

PDMS substrates were fabricated at a size of 10 cm (length) \times 3.5 cm (width) \times 2 mm (thickness). The LBL composite was formed on PDMS by cyclically immersing the PDMS into the sequential deposition of oppositely charged polyelectrolytes (PEI) and SWNTs. The PEI absorption procedures were carried out at room temperature, and the SWNT absorption procedures occurred in a magnetic field at 8.5 Tesla (T).

During the LBL/alignment process, we first immersed the PDMS substrate into the 0.5% PEI aqueous solution for 10 min, then washed it three times with DI water and dried under a N₂ gas flow. The PEI-coated PDMS was immersed into the SWNT–NaDDBS solution placed in the 8.5 T magnetic field for 10 min, and then removed from the beaker and dried in the magnetic field to maintain the alignment. It was then washed by immersing it into the DI water 3 times. Repeating the above procedures to the desired repeating cycles, the [SWNT–NaDDBS/PEI]n multilayer composites were fabricated on the PDMS substrate. The fabricated composite film could then be removed from the PDMS substrate to any other solid substrate (metals, quartz, glass etc) for further tests.

2.3. Characterization

An 8.5 T magnet was provided by the National High Magnetic Field Laboratory (NHMFL). The UV–vis spectra were obtained using a Cary 5000 machine (Varian Inc.) at a range of 200–800 nm wavelength to reveal layer structures. Tests were carried out by depositing the SWNT–NaDDBS and PEI on quartz slides alternately. The deposition procedure was the same as the composite fabrication procedure. The UV–vis detection was carried out after each of the 4 cycles assembled.

The quartz crystal microbalance (QCM) measurements were performed with Au resonators by QCM 200 (Stanford Research Systems, Inc.). The optical microscopy used in our experiments was the Olympus BS 40. An inVia Raman Microscope (Renishaw Inc.) was used for Raman spectrum analysis. The major parameters were laser wavelength: 785 nm, laser gate: 1200 l mm⁻¹, exposure time: 100 s, and laser power level: 0.2%. SEM measurements were conducted at an accelerating voltage of 10 kV on a JEOL JSM-7401F FE-SEM. The resistivity measurement was taken by using a standard four-probe method. A KEITHLEY 2410 meter was used as the source meter for the measurement.

3. Results and discussion

3.1. Layer-by-layer structures and thickness

The assembly of SWNT/PEI multilayer composites was examined by using UV–vis absorption spectroscopy. Figure 2 shows that the UV–vis spectra of the SWNT/PEI multilayer composites confirm that UV absorption increased as the number of bilayers increased. An absorption peak of 277 nm of the spectra proves the containment of SWNTs in the composites, as previously described [37]. The linear increase of spectrum intensity in the inset figure further confirms a reproducible growth of SWNT layers from cycle to cycle. Every four dipping cycle resulted in the deposition of the same amount of nanotubes in the composites, which was further quantified and confirmed by QCM analysis, as described late.

Figure 3 displays a QCM frequency shift with the same assembled step of PEI and SWNT–NaDDBS deposition on the substrate. The absorption rates of PEI (\bullet) and SWNT–NaDDBS (\blacksquare) in each cycle were similar. This means that in



Figure 2. UV–vis spectra of [SWNT–NaDDBS/PEI]n (n = 4–20) LBL assembled composites on a quartz slide; the UV–vis spectra were measured after each of 4 cycles. Inset drawing shows a plot of the absorbance at 267 nm versus the layer number (n).

each bilayer, the weight of PEI and SWNT–NaDDBS is the same and can be calculated;

$$\frac{\mathrm{d}m}{\mathrm{d}n}(\mathrm{PEI}) = \frac{\mathrm{d}m}{\mathrm{d}n}(\mathrm{SWNT} - \mathrm{NaDDBS}) = 15 \ \mu \mathrm{g \ cm^{-2}}.$$
 (1)

This suggests that the concentration of SWNT–NaDDBS was about 50 wt%—much higher than common composites fabricated by a traditional method, such as resin/SWNT mixing approach. The QCM results also suggest the uniform loading of the nanotubes within each layer, which is consistent with the UV–vis spectra analysis shown in figure 1. As shown in table 1, the first bilayer of the assembly was higher than the rear bilayers, while the average mass of each bilayer was about 30 μ g cm⁻².

Figure 4 shows a cross-sectional view of a SWNT-NaDDBS/PEI multilayer composite sample. This demonstrates a relatively uniform multilayer structure of the LBL composite film on the PDMS substrate (as shown by figure 4(A)). During preparation of the cross-sections of the PEI/SWNT multilayer samples in our experiments, there were many CNT pull-outs. That makes difficult to clearly see the multilayer structures. The SEM images in figures 4(B) and (C)display the relationship between the number of bilayers and the thickness of the [SWNT-NaDDBS/PEI]n LBL assembled multilayer composite sample. The composites contained a LBL multilayer structure. We used two samples with a different numbers of bilayers to further evaluate layer thickness uniformity. Sample A was assembled with 25 cycles, and sample B was 10 cycles. As the scale bars showed in the SEM images, the thickness of the first composite sample was about 3.5 μ m, so each SWNT-NaDDBS/PEI bilayer thickness was about 140 nm. The thickness of the second sample was nearly 1.5 μ m. Each bilayer thickness was also ~ 150 nm, verifying the uniform thickness of the layers. Based on multiple measurements, each SWNT-NaDDBS/PEI bilayer can be estimated to have the same thickness at around



Figure 3. QCM mass shifts with alternative absorption step during the deposition of SWNT–NaDDBS/PEI multilayer composite on the substrate; the first layer is coated with PEI, then with SWNT–NaDDBS.

Table 1. Conductivities of SWNT-NaDDBS/PEI LBL composites.

	Resistance (MΩ)	Length (mm)	Thickness (µm)	Width (mm)	Resistivity (Ω m)
Sample 1	0.85	5.7	3.1	4.1	2.17
Sample 2	0.5	4.1	3.1	5.7	2.15
Sample 3	4.5	9.1	1.05	5.5	2.86
Sample 4	1.67	5.5	1.05	9.1	2.90

 150 ± 10 nm. The reason the bilayer thickness is much larger than that of the monolayer SWNT (rope diameters about 20–30 nm) film is due to the interstices structures between the SWNTs. The SWNTs were not well-packed in-plane within the nanotube layers to form a monolayer due to the large and non-uniform SWNT rope size and imperfect alignment, which led to many interstices between the SWNTs.

3.2. SWNT alignment

The degree of alignment of SWNTs in the multilayer composites was analyzed by Raman spectroscopy. This characterization relies on the fact that the Raman intensity of the tangential vibration mode (G band) of SWNTs is sensitive to Raman polarizer angle [11]. The tangential mode intensity reached a maximum when the polarized light was parallel to the nanotubes' axis and decreased gradually as the angle of the polarizer moved away from 0° (parallel to the nanotubes' axis) to 90° (perpendicular to the nanotubes' axis). Figure 5 shows the tangential peaks of the polarized Raman spectra for the multilayer composites for a series of angles. As expected, the maximum intensity was observed when the polarized light was parallel to the applied magnetic field direction (0°) , and the smallest intensity appeared when the polarized light was perpendicular to the magnetic field direction (90°). The Raman results demonstrate the preferential alignment of the SWNTs along the magnetic alignment direction.

Optical microscopy was also used for an initial qualitative evaluation of the degree of alignment. Figure 6(A) shows



Figure 4. SEM images of the cross-sections of SWNT–NaDDBS/PEI multilayer composite showing multilayer structures.

an optical micrograph of a SWNT–NaDDBS/PEI multilayer composite sample aligned in a magnetic field of 8.5 T. The composite sample showed good nanotube alignment in a relatively large area. A high magnification microscope image (figure 6(B)) further proves that the aligned composite contains relatively uniformly aligned SWNT bundles along the magnetic field direction.

The SEM images of the outermost SWNT layer of the LBL assembly multilayer composite clearly demonstrate



Figure 5. Raman spectra showing tangential peak shift of SWNTs aligned by magnetic field.



Figure 6. Optical micrographs of SWNT–NaDDBS/PEI multilayer composites.

substantial alignment (figure 7). Figure 7 shows that many SWNTs did not exactly follow magnetic force (MF) direction indicated in the image. This is probably due to the inability to maintain the substrate orientation exactly the same for reach deposition since the substrate was manually placed into



Figure 7. SEM images of aligned SWNTs by magnetic field and the outermost surface of the LBL composites.

magnet field. Better alignment consistency could be achieved by developing more reliable fixtures to ensure the substrate orientation in magnetic field.

3.3. Electrical conductivity

The electrical resistance of the LBL assembled SWNT– NaDDBS/PEI multilayer composites was measured and results are provided in table 1. The electrical resistivity was calculated based on the equation (2)

$$\gamma = \frac{1}{\rho} = \frac{1}{R} \times \frac{\text{length}}{\text{width} \times \text{thickness}}.$$
 (2)

Here, γ , ρ and *R* are conductivity, resistivity and resistance, respectively. LBL samples showed a high resistivity, 2–3 Ω m along the alignment direction, lower than the high SWNT loading carbon nanotube buckypaper composites [41]. We believe that the reason why the random buckypaper composites are high conductive is due to better contacts between CNTs because of good entanglement and more direct tube to tube interactions. In our PEI/SWNT multilayer samples, nanotube alignment and surfactant may reduce entanglement and contacts; hence reduce the conductivity of the samples. The LBL films with multiple alignment directions and less residual surfactant to improve tube to tube contacts should improve conductivity.

Highly ordered LBL SWNTs/polymer multilayer composites on the flexible PDMS substrate can lead to various potential applications. Since they are ultrathin, such composites can remain conformal and well-adhered, even on a highly deformed PDMS substrate. This interesting result indicates the possibility to design flexible composites, optical and electrical devices, and deformable energy storage and conversion devices. Since PDMS is a very common stamp material in micro-contact lithography, the multilayer composites on the PDMS substrate can be easily transferred to any other substrates for different applications.

4. Conclusion

In this research, we demonstrated that SWNTs can be successfully aligned in a magnetic field and assembled with PEI through a layer-by-layer approach to fabricate SWNT-NaDDBS/PEI composites. Such multilayer composite structures were constructed with alternating polyelectrolyte. The SWNT layers were constructed by electrostatic absorption. The UV-vis, QCM and SEM images prove that the assembly of SWNTs and PEI layers had the same deposition amount, which ensures the high SWNT concentration and homogeneous distribution in the nanocomposite. Each deposition bilayer thickness was uniform. Strict thickness control and good nanotube alignment were achieved. Further studies to optimize the process and use different sizes of SWNTs, MWNTs, and carbon nanofibers should lead to the potential to make highly ordered nanofiller packing and alignment, leading to more complex three-dimensional nanostructures, such as crossbars and hierarchically arranged nanoscale building blocks for developing novel sensors and devices.

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