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Single-Walled Carbon Nanotubes Spontaneous Loading into Exponentially Grown LBL Films

Sudhanshu Srivastava,[†] Paul Podsiadlo,^{†,‡} Kevin Critchley,[†] Jian Zhu,[†] Ming Qin,[†]
Bong Sup Shim,[†] and Nicholas A. Kotov^{*,†}

[†]Departments of Chemical Engineering, Materials Science and Engineering, Biomedical Engineering, University of Michigan, Ann Arbor, Michigan 48109, and [‡]Center for Nanoscale Materials, Argonne National Laboratory, Argonne, Illinois 60439

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Exponentially growing layer-by-layer (e-LBL) assembled films attracts a lot of attention mostly due to multiple practical applications in biology and medicine. However, e-LBL was observed only for a very limited number of polymers. This fact inevitably limits the area of research and functionalities that one can obtain for them. Also, it is fundamentally important to gain better understanding of the effect and importance of molecular flexibility for e-LBL films. Here we report that dispersions of rod-like nanocolloids such as single walled carbon nanotubes (SWNTs) and nanowires (NWs) can spontaneously “bore into” and stay in the e-LBL matrix. Molecular rigidity and surface charge appear to be the key parameters determining the possibility of such a process and its extent. SWNT forms a thick 2–25 μm penetration layer, while insufficient flexibility leads to hedgehog structures in the case of CdTe and Te NWs. Electrical properties of the films obtained display fundamental differences with SWNT composites made by standard methods. They were attributed to thermal activation of vibrational modes of film components disturbing nanotube-to-nanotube tunneling. The dynamic nature of the e-LBL film combined with unique SWNTs properties can lead to a new type of smart materials and can help a better understanding of methods of morphological control in nanocomposites.

Advancement in the layer-by-layer (LBL)¹ assembly has recently been devoted to the fabrication of nanostructured multilayers whose thicknesses increase exponentially with the number of deposited layers.² This behavior results from the diffusion of at least one of the two polymer chains through the whole film thickness at each bilayer deposition step.³ Exponential layer-by-layer (e-LBL)⁴ films have gained intense interest because of their dynamic nature associated with “in-and-out” diffusion of flexible polymers allowing incorporation of nanoscale species in a controlled fashion. The e-LBL was only realized previously for selected polymers with highly flexible chains to incorporate small ions,⁵ organic dyes,⁶

and drug molecules.⁷ So, an important fundamental question arises whether the utilization of the fast growth rate of e-LBL is possible for one-dimensional (1D) inorganic nanoscale colloids, such as nanorods,⁸ nanotubes,⁹ and nanowires (NWs),¹⁰ which display a certain degree of mobility and flexibility and have some similarity with rodlike polymers. From a practical stand point, the answer to this question is also important. Incorporation of 1D nanocolloids in the already prepared LBL film can lead to unique composite materials that combine both dynamics of exponentially growing polymer blends and special electrical/optical/magnetic/mechanical characteristics of the 1D nanostructures. Such properties can be exemplified by highly networked mechanically robust materials¹¹ with very unusual conductance, reflection, and optoelectronic responses.¹² Among these materials, multi- and single-walled carbon nanotubes (SWNTs) and their organized assemblies¹³

*Corresponding author. E-mail: kotov@umich.edu.

- (1) (a) Decher, G. *Science* **1997**, 277, 1232–1237. (b) Ariga, K.; Hill, J. P.; Ji, Q. *Phys. Chem. Chem. Phys.* **2007**, 9, 2319. (c) Ariga, K.; Hill, J. P.; Lee, M. V.; Vinu, A.; Charvet, R.; Acharya, S. *Sci. Technol. Adv. Mater.* **2008**, 9, 014109.
- (2) Picart, C.; Lavallo, P.; Hubert, P.; Cuisinier, F. J. G.; Decher, G.; Schaaf, P.; Voegel, J. C. *Langmuir* **2001**, 17, 7414.
- (3) (a) Picart, C.; Mutterer, J.; Richert, L.; Luo, Y.; Prestwich, G. D.; Schaaf, P.; Voegel, J. C.; Lavallo, P. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, 99, 12531. (b) Lavallo, P.; Vivet, V.; Jessel, N.; Decher, G.; Voegel, J. C.; Mesini, P. J.; Schaaf, P. *Macromol* **2004**, 37, 1159.
- (4) Ball, V.; Hübsch, E.; Schweiss, R.; Voegel, J. C.; Schaaf, P.; Knoll, W. *Langmuir* **2005**, 21, 8526.
- (5) Hübsch, E.; Fleith, G.; Fattison, J.; Labbé, P.; Voegel, J.-C.; Schaaf, P.; Ball, V. *Langmuir* **2005**, 21, 3664.
- (6) Burke, S. E.; Barrett, C. J. *Macromolecules* **2004**, 37, 5375.
- (7) Vodouhê, C.; Le Guen, E.; Mendez Garza, J.; Francius, G.; Déjugnat, C.; Ogier, J.; Schaaf, P.; Voegel, J. C.; Lavallo, P. *Biomaterials* **2006**, 27, 4149.

- (8) Vial, S.; Pastoriza-Santos, I.; Perez-Juste, J.; Liz-Marzan, L. M. *Langmuir* **2007**, 23, 4606–4611.
- (9) Mayya, K. S.; Gittins, D. I.; Dibaj, A. M.; Caruso, F. *Nano Lett.* **2001**, 1, 727–730.
- (10) Guo, Y. G.; Wan, L. J.; Bai, C. L. *J. Phys. Chem. B* **2003**, 107, 5441–5444.
- (11) Mamedov, A. A.; Kotov, N. A.; Prato, M.; Guldi, D. M.; Wicksted, J. P.; Hirsch, A. *Nat. Mater.* **2002**, 1, 190–194.
- (12) Wang, Y.; Tang, Z. Y.; Podsiadlo, P.; Kotov, N. A. *Adv. Mater.* **2006**, 18, 518–522.
- (13) Correa-Duarte, M. A.; Grzelczak, M.; Salgueirino-Maceira, V.; Giersig, M.; Liz-Marzan, L. M.; Farle, M.; Sieradzki, K.; Diaz, R. *J. Phys. Chem. B* **2005**, 109, 19060.

offer particularly significant promise for overcoming technical challenges in membrane electrodes, fuel cells,¹⁴ flexible electronics,^{15,16} and ultrastrong composites^{11,15} because of exceptionally high tensile strength (37 TPa), Young's modulus (1.1 TPa),¹⁷ and electrical conductivities (1 to $\sim 3 \times 10^6$ S/m).¹⁸ The combination of these properties and high mass transfer rate is considered to be the key for solving the challenges of sensors, separation media, biomaterials, and energy applications. Specifically, increasing strength and stiffness while retaining high flux of matter is vital for desalination membranes, lithium batteries, and fuel cell electrodes. Asymmetrical membranes could be particularly beneficial for these processes. Also, drug release previously reported from e-LBL films can be made remotely controlled^{6,7} after infusion of conductive SWNTs. Potentially, all these advanced features can be realized using e-LBL films¹⁹ uniting high diffusion rates and SWNTs.

In this paper, we demonstrate that loading of SWNTs in the already prepared e-LBL films is possible, and moreover, they display unusually high internal mobilities resulting in deep spontaneous penetration into the matrix of e-LBL films. The study also revealed that SWNT properties remain stable even after the infusion in the LBL films. We used poly(diallyldimethyl ammonium chloride)/poly(acrylic acid), (PDDA/PAA)_n, e-LBL system, which previously demonstrated the incorporation of CdTe nanoparticles.²⁰ The films were prepared by dipping alternatively a glass substrate in 0.5% w/v PDDA and 1% w/v PAA solutions (Figure 1E). We note that the PDDA/PAA system undergoes extensive, pH-dependent swelling in aqueous conditions. Exponential growth for PDDA/PAA films also stipulates an increased mobility of the polymer chains in the films,^{2,4} which in turn opens the possibility for nanocolloids to penetrate inside them. To attempt SWNT incorporation, we used two negatively charged dispersions of CNTs stabilized with either sodium dodecyl sulfate (SDS), denoted as SWNT 1,²¹ or PAA denoted as SWNT 2.²² Positively charged SWNTs coated with CTAB (cetyltrimethylammonium bromide) and CdTe NWs were also investigated for comparative incorporation. As prepared (PDDA/PAA)_n, $n = 200$, (where n is the number of LBL deposition cycles) films, were exposed initially to SWNT 1 dispersion at pH 4.8.

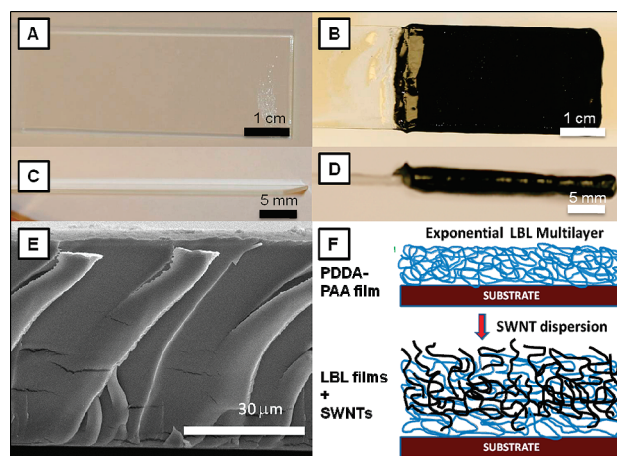


Figure 1. (A) PDDA/PAA LBL film on glass. (B) LBL film loaded with SDS-coated SWNTs for 1 day. (C) Side view of PDDA-PAA coated glass slide. (D) Side-view of swollen PDDA-PAA film loaded with SDS-coated SWNTs. (E) Cross-section of the (PDDA-PAA)₂₀₀ LBL film. (F) Schematics of incorporation of SWNTs in e-LBL films.

After just 2 h of contact with SWNT 1 solution (Figure 1D) without further treatment, the films turned completely black, with no aggregation being observed anywhere in solution. After 1 day of immersion, the LBL films were found to be highly swollen compared to original (PDDA/PAA)₂₀₀ (Figure 1B). Obviously, the SDS-coated SWNTs efficiently penetrate the films (Figure 1F). Moreover, no treatment at any pH resulted in their removal from the film. In contrast, experiments with positively charged SWNTs at pH 4.3 showed no evidence of incorporation in the LBL films. No in-depth incorporation was also observed for more rigid CdTe and Te NWs (pH 8.2) (see the Supporting Information) with comparable dimensions and negative charge similar to SWNT 1. However, hedgehog morphology of the film can be seen in the film surface with NW sticking out from the polyelectrolyte matrix (Figure S4 D, E, Supporting Information). Thus, rigidity and charge of nanocolloids are probably the key factors controlling their infusion in the e-LBL films.

To analyze the penetration depth and understand the kinetics of the penetration process, (PDDA/PAA)₂₀₀ films were kept in contact with SWNT 1 for 6 h, 24 h, and 7 days. All the swollen films loaded with SWNT 1 were dried for 3 h under constant flow of air prior to being analyzed by the scanning electron microscopy (SEM). The cross-section of the films under SEM displayed clear morphological change in the (PDDA/PAA)₂₀₀ before, (Figure 1E) and after loading with SWNT 1 (Figure 2C). The cross-section of the films showed sequential increase in the penetration of SWNT 1 in the LBL films with 1–2 μm after 6 h, 4–5 μm after 24 h and 20–25 μm after 7 days, respectively, depending on the time of SWNT loading (Figure 2A–C). These data also indicate that films are strongly asymmetric, which is important for fuel cells and electrical devices. Correspondingly, electrical resistance, R , measurements carried out on air-dried films with loading intervals of 6, 12, 24, and 36 h and 7 days showed a drastic decrease in sample

- (14) Michel, M.; Taylor, A.; Sekol, R.; Podsiadlo, P.; Ho, P.; Kotov, N. A.; Thompson, L. *Adv. Mater.* **2007**, *19*, 3859.
- (15) (a) Shim, B. S.; Tang, Z.; Morabito, M. P.; Agarwal, A.; Hong, H.; Kotov, N. A. *Chem. Mater.* **2007**, *19*, 5467–5474. (b) Pan, C.; Ge, L. Q.; Gu, Z. Z. *Compos. Sci. Technol.* **2007**, *67*, 3271.
- (16) Xue, W.; Liu, Y.; Cui, T. H. *Appl. Phys. Lett.* **2006**, *163512*.
- (17) Baughman, R. H.; Zakhidov, A. A.; de Heer, W. A. *Science* **2002**, *297*, 787.
- (18) Thess, A.; Lee, R.; Nikolaev, P.; Dai, H.; Petit, P.; Robert, J.; Xu, C.; Lee, Y. H.; Kim, S. G. *Science* **1996**, *273*(5274), 483.
- (19) Yoo, P. J.; Nam, K. T.; Qi, J. F.; Lee, S. K.; Park, J.; Belcher, A. M.; Hammond, P. T. *Nat. Mater.* **2006**, *5*, 234.
- (20) Srivastava, S.; Ball, V.; Podsiadlo, P.; Lee, J.; Ho, P.; Kotov, N. A. *J. Am. Chem. Soc.* **2008**, *130*, 3748.
- (21) O'Connell, M. J.; Bachilo, S. M.; Huffman, C. B.; Moore, V. C.; Strano, M. S.; Haroz, E. H.; Rialon, K. L.; Boul, P. J.; Noon, W. H.; Kittrell, C.; Ma, J.; Hauge, R. H. *Science* **2002**, *297*, 593.
- (22) Ning, J. W.; Zhang, J. J.; Pan, Y. B.; Guo, J. K. *Ceram. Int.* **2004**, *30*, 63–67.

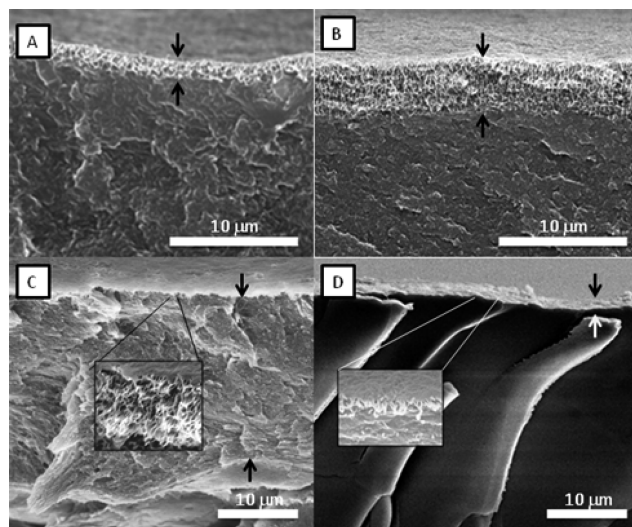


Figure 2. Cross-sectional SEM images of (PDDA/PAA)₂₀₀ films loaded with SWNTs. (A) SDS-coated SWNTs after 6 h loading. (B) SDS-coated SWNTs after 24 h. (C) SDS-coated SWNTs after 7 day loading. Insert shows the high-resolution image of SWNT penetration zone. (D) PAA-coated SWNTs after 7 day loading.

surface resistance with an increase in the exposure time. The obtained resistance values per square area were 260, 170, 67, 31, and 3 k Ω /sq, respectively. With higher loadings of nanotubes, the conductivity obviously increases because of more extensive SWNT network. It can be a convenient way of preparation of conductive coatings. SWNT 2 infiltrating in (PDDA/PAA)₂₀₀ films demonstrated the same trend albeit with lower electrical conductance. They showed resistance of 5.3 M Ω /sq and 4.2 M Ω /sq being exposed for 24 h and 7 days (*pH* 3.1), respectively. From SEM, SWNT 2 were mainly localized on the top surface of the film within \sim 2–3 μ m, whereas SWNT 1 showed penetration to the depth of \sim 20–25 μ m (Figure 2C, D), which explains the difference in electrical properties. The molecular reasons for much higher potency of SWNT 1 for penetrating the PDDA/PAA films than the SWNT 2 are not completely understood and may be associated with both greater flexibility of SDS coated SWNTs vs those coated with PAA or stronger hydrogen bonds between PAA and/or the multilayer matrix.

In the top layer of penetration, both SWNT 1 and 2 seemed to be blended with the polymers or not penetrating through the complete film. The SEM images taken at different levels of the cross-section and close-ups did show the gradient infusion of SWNT 1 through the films in 7 days (see Supporting Information). To further confirm the lodging of SWNT 1 deep inside of the film, we introduced a “free-standing” (PDDA/PAA)₂₀₀ film (\sim 60 μ m in thickness) into the SWNT 1 dispersion for \sim 7 days, allowing the SWNTs to “bore-in” from both sides of the film (See Supporting Information). This allowed the SWNTs to be incorporated throughout the film thickness. Electrical measurements through the cross-section of the free-standing films showed resistivity

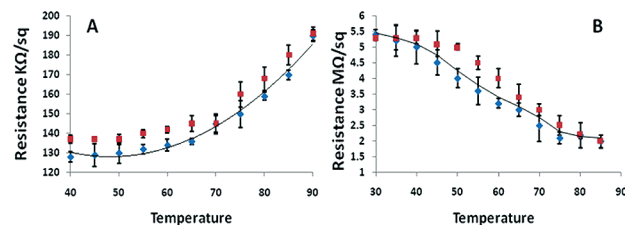


Figure 3. Temperature dependence of area resistance for e-LBL films with incorporated (A) SWNT 1 and (B) SWNT 2. Blue dots indicate the trend upon increasing the temperature values and red dots indicate the reversible trend of the resistance values upon cooling. After the samples were cooled, the resistance values showed a reversible trend.

of 5 k Ω ·m indicating efficient insertion of SDS-coated CNTs through the entire film.²³ SWNTs although were not prominently visible in the middle region of the film, but some portions of the film show up to a depth of \sim 25 μ m CNTs infusion (see the Supporting Information). The gradient of local loading can be an interesting property that can be potentially used in actuators and other electrical devices.

The LBL films loaded with SWNTs were further investigated in respect to their electrical properties. In particular, we were interested in the change of their resistance, R , with temperature, T , because (1) it has a strong relationship to the dynamics of the internal structure of the material and (2) it is obviously important to understand the trends for applications mentioned above. The films selected for the study were kept in contact with SWNTs for about 20 h and were dried under a continuous flow of air. SWNT 1 loaded film showed an increase in the surface resistance values from 129 k Ω /sq at 40 $^{\circ}$ C to 190 k Ω /sq at 90 $^{\circ}$ C (Figure 3A), i.e., positive $\partial R/\partial T$. Importantly, the temperature dependence was completely reversible and the surface resistance values returned to 136 k Ω /sq upon cooling. The cycle can be repeated as many times as necessary without significant change in the curves, indicating that the observed trend is not the effect of drying. The films prepared by loading of SWNT 2 presented the opposite but similarly reversible trend. Resistance was observed to decrease with T from 5.5 M Ω /sq at 30 $^{\circ}$ C to 2 M Ω /sq at 85 $^{\circ}$ C (Figure 3B). For comparison, we also measured the temperature dependence of SWNT LBL films with polyvinyl alcohol (PVA) prepared by LBL assembly using linear film growth which also revealed negative $\partial R/\partial T$ (see the Supporting Information, Figure S6).

Importantly, the I – V curves²⁴ of all samples showed almost perfect linear Ohmic behavior with 4.6 k Ω and 4.0 M Ω for SWNT 1 and 2, respectively. This means that the effect of Schottky resistance at contacts is negligible and the dependences should be attributed to the conductance in the nanotube material (See Supporting Information). This observation allows us to conclude that the surface region with high local concentration of SWNTs determines the charge transport in (PDDA/PAA)₂₀₀ films infiltrated with SWNT 1. The mechanism

(23) The experiment was performed after complete drying for 3 h.

(24) Tarkiainen, R.; Ahlskog, M.; Penttilä, J.; Roschier, L.; Hakonen, P.; Paalanen, M.; Sonin, E. *Phys. Rev. B* **2001**, *64*, 195412.

of electrical conductivity there might be attributed to interrupted metallic transport,²⁵ although semiconducting SWNTs can also make pivotal contribution determining $\partial R/\partial T$.

In general, the conductivity of low volume fraction ($<0.6\%$) CNT/polymer nanocomposites typically increase as a function of temperature,²⁶ that is the same as displayed in all cases studied here but SWNT 1 e-LBL films. There have been studies that have shown that polymer softening above 220 °C caused a slight decrease in conductivity before returning to the increasing trend near 300 °C; however, these temperatures are much higher than those used in this study and therefore the arguments used may not explain the temperature response observed in this study.²⁷ Among other cases of SWNT materials, positive $\partial R/\partial T$ was observed for buckypapers.²⁵

The increase, or decrease, in the resistance with rising temperature for SWNT 1 and 2 is typically discussed in terms of metallic or semiconducting behavior^{25a} of the films, respectively.^{15,28} However, this idea probably cannot explain the difference in $\partial R/\partial T$ data for SWNT 1 and 2 in this study. We assume that there is no separation of metallic and semiconducting SWNTs in the e-LBL films. Although the preferential incorporation of either metallic or semiconducting SWNTs is possible and would be exceptionally interesting, we do not see the structural grounds for this process to occur at the moment. Note also that the absolute value of resistivity and total loading are obviously not the discriminating factors for determining the temperature dependence because classical LBL of PVA-SWNT films and SWNT 1 e-LBL films have equally high conductivity but different $\partial R/\partial T$ trends. In all cases, it is also safe to assume (Figure 2) that SWNT loading is above the percolation threshold.¹¹ With these assumptions, the explanation of unusual $\partial R/\partial T$ trend can be found in different dynamics of the conducting matrixes for different LBL films. The classical LBL (see the Sup-

porting Information) and SWNT 2 e-LBL (Figure 3B) films produce more constrained molecular system with little freedom of movement. On the basis of previous data, this is clearly the case with classical LBL films.¹¹ A lower degree of penetration of nanotubes in Figure 2D indicates that this also holds true for SWNT 2 e-LBL system. So, the reason for the opposite trend of $\partial R/\partial T$ in SWNT 1 e-LBL (Figure 3A) is that higher T substantially increases the mobility of the SWNTs in the LBL composites. Even a small increase in local vibrations at SWNT junctions in more flexible system can result in a very significant decrease of tunneling efficiencies because of the exponential dependence of the tunneling current on temperature and gap distance, which we indeed observe in Figure 3A. For classical LBL films and Figure 3B, the temperature dependence in this range is governed not by the dynamics of junctions but rather by the transport in the tubes themselves. Because preferential conductive pathways lie mostly via metallic tubes, the negative $\partial R/\partial T$ slope is observed.

In conclusion, we demonstrated the penetration of the SWNTs in already-prepared exponential LBL films. Molecular rigidity and surface charge appear to be the key parameters determining the possibility of long axial nanocolloids to "bore into" the exponential LBL films. Insufficient flexibility leads to hedgehog structures on the surface of the film, as in the case of CdTe and Te NWs. Electrical properties of the films obtained display fundamental differences with SWNT composites made by standard LBL approach attributed to thermal activation of vibrational modes of film components disturbing nanotube-to-nanotube tunneling. The described process will substantially accelerate preparation of LBL films of nanotubes. The dynamic nature of the e-LBL film combined with unique SWNTs properties will lead to new type of smart materials.

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Supporting Information Available: Experimental details and additional figures (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

- (25) (a) Skakalova, V.; Kaiser, A. B.; Dettlaff-Weglikowska, U.; Hrnčarikova, K.; Ruth, S. J. *Phys. Chem. B* **2005**, *109*, 7174. (b) Dettlaff-Weglikowska, U.; Skakalova, V.; Meyer, J.; Cech, J.; Mueller, B. G.; Roth, S. *Curr. Appl. Phys.* **2007**, *7*, 42.
- (26) Simsek, Y.; Ozyuzer, L.; Seyhan, A. T.; Tanoglu, M.; Schulte, K. J. *Mater. Sci.* **2007**, *42*, 9689.
- (27) Yang, J.; Xu, T.; Lu, A.; Zhang, Q.; Fu, Q. *J. Appl. Polym. Sci.* **2008**, *109*, 720.
- (28) (a) Zhang, M.; Fang, S. L.; Zakhidov, A. A.; Lee, S. B.; Aliev, A. E.; Williams, C. D.; Atkinson, K. R.; Baughman, R. H. *Science* **2005**, *309*, 1215. (b) Yang, X. B.; Ni, J. *Phys. Rev. B* **2005**, *71*, 165438.