Communication

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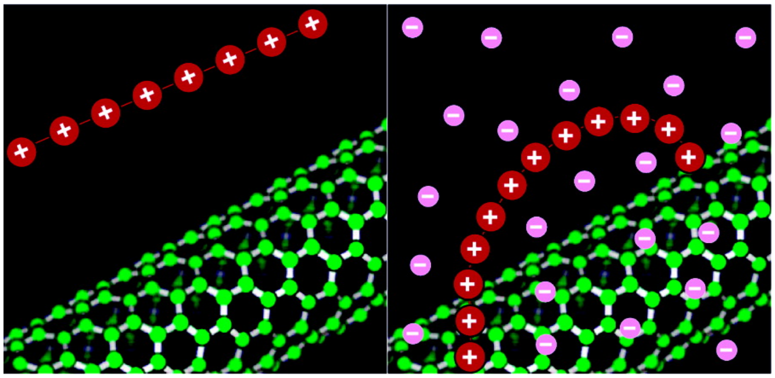

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Persistence Length Control of the Polyelectrolyte Layer-by-Layer Self-Assembly on Carbon Nanotubes

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One-dimensional inorganic materials, such as carbon nanotubes[1] and semiconductor nanowires,[2,3] have been central to recent advances in materials science. Unique mechanical and electronic properties of these materials enabled a variety of applications ranging from novel composites,[4] to electronic circuits,[5] to sensors.[6] Often, these applications require noncovalent modification of carbon nanotubes with organic compounds,[7] DNA and biomolecules,[8] and polymers.[9] We recently demonstrated a versatile and flexible strategy for nanotube modification using layer-by-layer self-assembly of polyelectrolytes.[10] Researchers used this technique extensively for modification of flat surfaces[11] and micro-[12] and nanoparticles;[13] however, little is known about the mechanism and the factors influencing layer-by-layer self-assembly in one-dimensional nanostructures.

The exact conformation of polyelectrolyte chains deposited on single-walled carbon nanotubes (SWNT) is still unknown. There are two possible configurations: flexible polymers wrapping around the nanotube, and stretched, rigid chains stacked parallel to the nanotube axis.[9] Several factors, such as polymer rigidity, surface curvature, and strength of polymer−surface interactions, can determine the nature of assembly.[14−16] Persistence length of the polymer chain should be one of the critical parameters since it determines the chain's ability to wrap around the nanotube. Indeed, computer simulations for spherical substrates show that polymer rigidity and substrate surface curvature can influence the deposition process.[14,15] Computational models also show that the persistence length of the polymer must fall below the threshold values determined by target surface curvature in order to initiate polyelectrolyte deposition process.[17] Although these models described the effects of salt concentration and target surface curvature,[14,15] they considered only nanoparticles with a radius of 5 nm and larger.[16,18] One-dimensional materials, such as carbon nanotubes, provide an even more interesting template for studying self-assembly mechanisms since they give us access to even smaller surface curvatures down to 1 nm.

We have examined the role of the polymer persistence length in the layer-by-layer self-assembly process on carbon nanotubes by observing formation of multilayer polyelectrolyte shells around carbon nanotubes at different ionic strength. Persistence length of polyelectrolytes varies with solution ionic strength,[19] due to screening of the electrostatic repulsion between the polymer backbone charges;[20−23] therefore, changing ionic strength is a convenient way to alter the configuration of the polymer molecule systematically.

We have used the layer-by-layer self-assembly technique to form 5-layer thick coating of the alternating poly(allylamine hydrochloride) (PAH) and sodium poly(styrenesulfonate) (PSS) layers on the surfaces of the pristine single-wall carbon nanotubes. (We have also studied coating composed of PSS and poly(diallyldimethylammonium chloride) (PDDA); see Supporting Information for details.) For our experiments, we grew the nanotubes across copper TEM grid openings using catalytic chemical vapor deposition.[10] The polymer deposition solutions contained different amounts of NaCl to vary the ionic strength. After polymer multilayer formation, we examined the resulting coating in high-resolution TEM.

Figure 1 shows representative TEM images of coated nanotubes. Notably, we observed no continuous coatings on carbon nanotubes at low ionic strength (Figure 1A−C). For ion concentrations of 0.05−0.2 M, our samples contained more than 90% of bare uncoated single-walled nanotubes. Once the ionic strength became greater than 0.2 M, the polyelectrolytes formed a coating on about 85% of the nanotubes, with the thickness steadily increasing with the ion concentration (Figure 2). Researchers have previously described an increase of the polyelectrolyte layer thickness with the ionic strength for layer-by-layer assembly on flat surfaces;[25,26] however, they have not reported an ionic strength threshold for the deposition initiation.

Our results can be easily rationalized if we assume that the self-assembly mechanism involves wrapping of the polymer chains around the nanotubes. At low ionic strength, the polymer chains are too rigid to bend around the nanotube and the deposition cannot occur. Once the ionic strength is high enough to diminish the persistence length below the nanotube curvature (Figure 2 inset), the self-assembly can proceed and the polymer layers begin to form. Additionally, as the assembly diameter grows, the curvature effects diminish and self-assembly can proceed even at lower ionic strengths. We have found that, as long as the first three layers were deposited at high ionic strength, subsequent deposition steps could proceed at low ionic strengths (see Supporting Information). Moreover, unlike the individual single-wall nanotubes, larger-diameter single-walled nanotube bundles were usually coated by the polymers at all ionic strengths used in our studies (images not shown), further supporting our hypothesis.

We also note that we have previously reported polymer multilayer formation on carbon nanotubes at ionic strength below the deposition threshold.[10] However, those experiments utilized nanotube surface pretreatment with ionic pyrene derivatives to create surface charge on the nanotube, while the experiments reported here did not use pretreatment. In addition, in the present experiments, we

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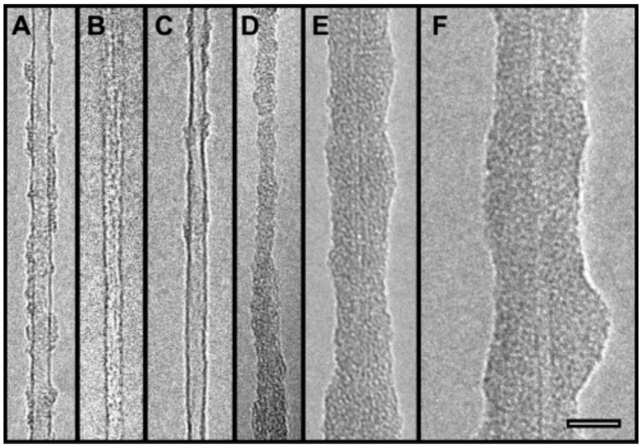

Figure 1. TEM images of single-walled carbon nanotubes after polymer deposition for ionic strengths of (A) 0.05 M, (B) 0.1 M, (C) 0.2 M, (D) 0.4 M, (E) 0.65 M, and (F) 1.05 M. Scale bar corresponds to 10 nm.

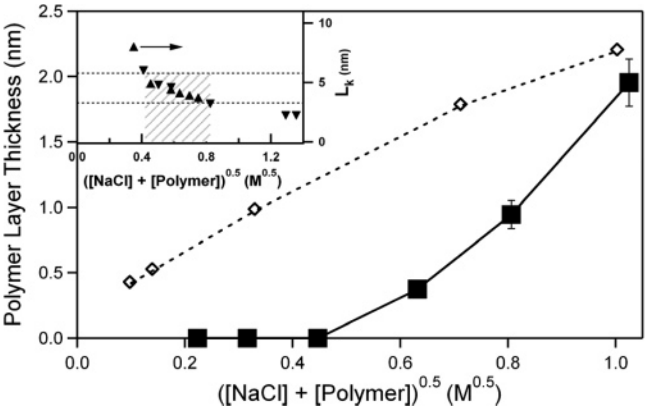

Figure 2. Average measured polymer thickness per layer of polyelectrolyte (■) on carbon nanotube surfaces as a function of electrolyte concentration. Experimental data for floating multilayers of the same polymer pair (PAH/PSS) (◇) are shown for comparison.[24] (Inset) Experimental data for PSS persistence length (L_K) as a function of electrolyte concentration (▲,[19]▼[23]). Dashed lines indicate the upper and lower boundary for the half-circumference of carbon nanotubes used in our experiments. Shaded area corresponds to the electrolyte concentration region, where persistence length crosses these boundaries.

have always found a small number of coated nanotubes even at low ionic strengths. These nanotubes, as well as small bundles of two or three SWCNTs, which are coated at any ionic strength, could have also contributed to the previously reported result.

To examine the link between chain conformation and polyelectrolyte layer-by-layer self-assembly on carbon nanotubes, we have compared the average coating thickness obtained in our experiments with the literature data for floating PAH/PSS polymer multilayers.[24] This comparison (Figure 2) shows that at all ionic strengths polyelectrolytes form thinner layers on the nanotube and that the coating thickness on the nanotubes begins to approach that on flat surfaces only at the high ionic strength of 1 M.

A comparison between the polymer persistence length data at different ionic strengths[19,23] and the size of our nanotubes provides further evidence for the wrapping mechanism of polymer self-assembly. Measured nanotube diameters in our experiments varied from 2.1 to 3.7 nm, which corresponds to a range of nanotube half-circumference shown in the inset of Figure 2. Remarkably, Figure 2 shows that the self-assembly process starts as soon as the polymer persistence length drops below the half-circumference of the nanotube. These data lend strong support for the self-assembly mechanism based on the polymer wrapping around the nanotube; as soon as the polymer chain can bend enough to match the nanotube surface curvature, the assembly process starts. This critical polymer chain curvature determines the threshold value of the ionic strength at which layer-by-layer self-assembly can proceed. We also argue that an alternative mechanism based on rodlike assembly is much less likely to produce this behavior, and even if it could, the correlation between assembly threshold and the nanotube persistence length would have been purely fortuitous.

Our results indicate that polymer conformation, or more specifically, the ability of the polymer chain to bend in order to accommodate the support curvature, is one of the critical parameters controlling layer-by-layer electrostatic self-assembly on one-dimensional templates. We also found that polymer rigidity at low ionic strength can suppress the polyelectrolyte assembly on carbon nanotubes. Our results indicate that this process likely involves wrapping of polymer chains around nanotubes. Thus, controlling the polymer chain conformation is a powerful strategy for fine-tuning self-assembly on one-dimensional templates.

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Supporting Information Available: Materials and Methods; additional experimental results on using different polycations and deposition conditions. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Baughman, R. H.; Zakhidov, A. A.; de Heer, W. A. *Science* **2002**, *297* (5582), 787−792.
(2) Hu, J. T.; Odom, T. W.; Lieber, C. M. *Acc. Chem. Res.* **1999**, *32* (5), 435−445.
(3) Xia, Y. N.; Yang, P. D.; Sun, Y. G.; Wu, Y. Y.; Mayers, B.; Gates, B.; Yin, Y. D.; Kim, F.; Yan, Y. Q. *Adv. Mater.* **2003**, *15* (5), 353−389.
(4) Dalton, A. B.; Collins, S.; Munoz, E.; Razal, J. M.; Ebron, V. H.; Ferraris, J. P.; Coleman, J. N.; Kim, B. G.; Baughman, R. H. *Nature* **2003**, *423* (6941), 703.
(5) Tans, S. J.; Verschueren, A. R. M.; Dekker, C. *Nature* **1998**, *393* (6680), 49−52.
(6) Kong, J.; Franklin, N. R.; Zhou, C. W.; Chapline, M. G.; Peng, S.; Cho, K. J.; Dai, H. J. *Science* **2000**, *287* (5453), 622−625.
(7) Chen, R. J.; Zhan, Y. G.; Wang, D. W.; Dai, H. J. *J. Am. Chem. Soc.* **2001**, *123* (16), 3838−3839.
(8) Katz, E.; Willner, I. *ChemPhysChem* **2004**, *5* (8), 1085−1104.
(9) O'Connell, M. J.; Boul, P.; Ericson, L. M.; Huffman, C.; Wang, Y. H.; Haroz, E.; Kuper, C.; Tour, J.; Ausman, K. D.; Smalley, R. E. *Chem. Phys. Lett.* **2001**, *342* (3−4), 265−271.
(10) Artyukhin, A. B.; Bakajin, O.; Stroeve, P.; Noy, A. *Langmuir* **2004**, *20* (4), 1442−1448.
(11) Decher, G. *Science* **1997**, *277* (5330), 1232−1237.
(12) Caruso, F.; Caruso, R. A.; Mohwald, H. *Science* **1998**, *282* (5391), 1111−1114.
(13) Gittins, D. I.; Caruso, F. *J. Phys. Chem. B* **2001**, *105* (29), 6846−6852.
(14) Stoll, S.; Chodanowski, P. *Macromolecules* **2002**, *35* (25), 9556−9562.
(15) Chodanowski, P.; Stoll, S. *J. Chem. Phys.* **2001**, *115* (10), 4951−4960.
(16) Netz, R. R.; Joanny, J. F. *Macromolecules* **1999**, *32* (26), 9013−9025.
(17) Manning, G. S. *J. Phys. Chem. B* **2003**, *107* (41), 11485−11490.
(18) Kunze, K. K.; Netz, R. R. *Phys. Rev. Lett.* **2000**, *85* (20), 4389−4392.
(19) Nierlich, M.; Boue, F.; Lapp, A.; Oberthur, R. *J. Physique* **1985**, *46* (4), 649−655.
(20) Brulet, A.; Boue, F.; Cotton, J. P. *J. Phys. II* **1996**, *6* (6), 885−891.
(21) Skolnick, J.; Fixman, M. *Macromolecules* **1977**, *10* (5), 944−948.
(22) Tricot, M. *Macromolecules* **1984**, *17* (9), 1698−1704.
(23) Spiteri, M. N.; Boue, F.; Lapp, A.; Cotton, J. P. *Phys. Rev. Lett.* **1996**, *77* (26), 5218−5220.
(24) Ruths, J.; Essler, F.; Decher, G.; Riegler, H. *Langmuir* **2000**, *16* (23), 8871−8878.
(25) Dubas, S. T.; Schlenoff, J. B. *Macromolecules* **1999**, *32* (24), 8153−8160.
(26) Ladam, G.; Schaad, P.; Voegel, J. C.; Schaaf, P.; Decher, G.; Cuisinier, F. *Langmuir* **2000**, *16* (3), 1249−1255.

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