

## **Layer-by-Layer Assembly of Single-Wall Carbon Nanotube Polymeric Nanocomposites: Structural Control and Material Properties**

*Bong Sup Shim<sup>1</sup>, Zhiyong Tang<sup>1</sup>, Vladimir Sinani<sup>1</sup>, Matthew Morabito<sup>1</sup>, Nicholas A. Kotov<sup>1,2</sup>*

*<sup>1</sup>Department of Chemical Engineering, University of Michigan, Ann Arbor, MI, 48109;*

*<sup>2</sup>Departments of Materials Science and Biomedical Engineering, University of Michigan, Ann Arbor, MI, 48109*

Single-wall carbon nanotubes (SWNTs) are widely acclaimed for their superior physicochemical properties. However, fabrication of high quality SWNT-polymer nanocomposites with corresponding properties of SWNTs has known to be very difficult due to lack of ability to control the molecular structure of the composites. In this scientific context, SWNT-polymer composites fabricated with layer-by-layer (LBL) assembly have been revealed to be promising because the technique allows for uniform dispersion and high loading of SWNTs in the polymeric matrix. Here, we introduce a SWNT - poly(styrene sulfonate) (PSS) - poly(vinyl alcohol) (PVA) nanocomposite fabricated by LBL assembly. We also demonstrate the ability to control the nanoarchitecture of this LBL assembly by “SWNT combing”, a technique developed to control the direction of SWNT alignments. The realized nanoarchitectures of the composites are directly observed by Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM). These molecularly controlled composites exhibit both excellent electrical conductivity and mechanical property with 50% of SWNT content. These material functionalities are found to be strongly affected by the molecular structure between SWNTs and polymer matrices as well as the properties of SWNTs.

## INTRODUCTION

Single-walled carbon nanotubes (SWNTs) have been extensively examined as additives to polymer nanocomposites in order to improve the composites' mechanical and electrical characteristics or to realize ultra strong and electrically conductive functional materials. In order to obtain superior functional properties for the fabricated SWNT-polymer composites, structural control of the building blocks at the molecular level is a primary objective. First, SWNTs should be homogeneously dispersed in the polymer matrix. From the standpoint of physical properties of a composite, it is desirable for each SWNT strand to form strong interconnections to the polymer matrix rather than maintaining weak van der Waals forces among SWNT strands in a bundle. Furthermore, if the SWNTs are well dispersed as electrically conductive fillers, then they can form numerous conductive percolation routes in a composite. Thus, the electrical conductivity of a composite can be improved simply by forming uniform SWNT dispersion in polymer matrix. In other words, homogeneity with uniformly dispersed multifunctional SWNTs in a polymer matrix becomes a critical feature for superior physical performance of a composite material. Second, SWNTs can be aligned in one direction in a composite. Exceptional physical and chemical properties of SWNTs are closely related to the anisotropic molecular structures of the embedded SWNTs - hollow tubular cylinders with a diameter of few nanometers and a length of a few micrometers. Therefore, the material functionality of a composite can be dramatically improved by controlling molecular alignment of SWNTs. For example, the record high strengths of SWNT composites are the result of a SWNT orientation<sup>1;2</sup>. Hence, physical properties of a composite can be further improved by aligning SWNTs in one direction from a randomly oriented state.

Layer-by-layer assembly (LBL) has demonstrated exceptional uniformity and versatility for constructing nano-structured composites with various nano-building blocks. (For more information, please see the reviews<sup>3;4</sup>.) In 2002, A. Mamedov *et al.* introduced an electrostatic LBL assembled nanocomposite fabricated with poly(ethylene imine) (PEI) and SWNTs. This nanocomposite showed promising mechanical properties by achieving uniform dispersion of SWNTs<sup>5</sup>. However, we introduce SWNT - poly(vinyl alcohol) (PVA) composites by hydrogen-bonding directed LBL assemblies which displayed improved mechanical and electrical properties. Moreover, we incorporate the SWNT combing technique into the LBL multilayer assemblies<sup>6</sup>. This method stretches and aligns SWNTs by air-water interfacial forces, allowing us to further improve the functional performances of the composites.

## **EXPERIMENTAL**

### **Materials.**

Poly(vinyl alcohol) (PVA, MW: 70,000 ~ 100,000) and Poly(sodium 4-styrene-sulfonate) (PSS, MW: 1,000,000) were purchased from Sigma-Aldrich Co. The purified HiPco single-wall carbon nanotubes (SWNTs) used for the experiment were purchased from Carbon Nanotechnologies Incorporated (CNI).

### **LBL assembly.**

Purified HiPco SWNTs were dispersed in 1 wt-% PSS solution with a 2 hr mild sonication in a VWR Model 150HT ultrasonic cleaner. The dispersion was centrifuged at 5000 rpm and then the supernatant was collected. 1 wt-% of PVA solution was prepared for another LBL partner. Each LBL layering process consists of 10 min dipping in the PVA or the SWNT solution, water rinsing, and drying. This procedure resulted in the deposition of a film with a layer sequence of  $[PVA/SWNT]_n$ , where  $n$  represents the number of repeated dipping processes in PVA and SWNT solutions. SWNT combing was performed by 15 psig of an air flow during this interim drying step following a water rinsing step. For a multilayered film with aligned SWNTs, the procedure included a high temperature annealing step at 200 °C for 10 min in order to fix the aligned structures.

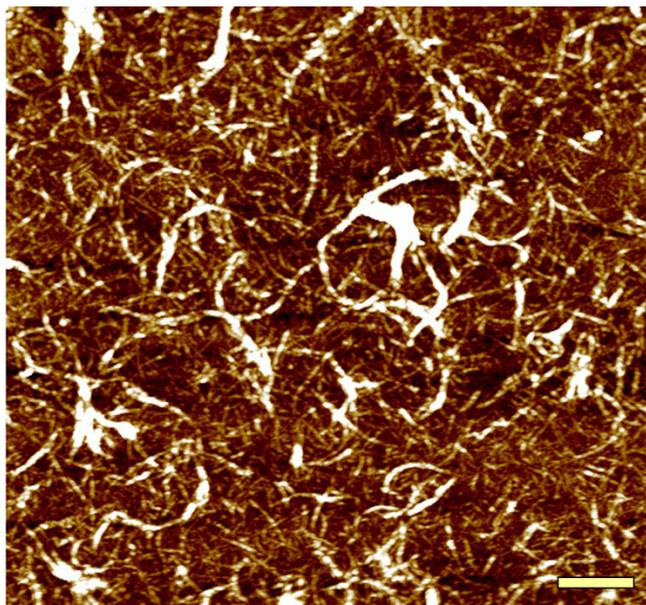
### **Instrumental analysis.**

Scanning electron microscopy (SEM) images were taken with a Philips XL30 Field Emission Gun Scanning Electron Microscope and a FEI Nova Nanolab Dualbeam FIB and Scanning Electron Microscope. Atomic force microscopy (AFM) imaging was performed with Nanoscope III (Digital Instruments/Veeco Metrology Group). UV-vis absorption measurements were taken using an Agilent 8453E UV-visible spectrometer.

## **RESULTS and DISCUSSION**

SWNT-polymer nanocomposites fabricated by LBL assemblies showed an exceptionally high uniformity of SWNT dispersion in the polymer matrix. The level of composites' uniformity is directly associated with the quality of a SWNT dispersion in solution state. Preparation of stable and single stranded SWNT dispersion in solution state has been widely investigated so that we can easily obtain well exfoliated SWNT dispersions without severe bundling. Here, we used PSS to prepare colloidal stability of SWNT dispersions, as opposed to mechanical stability<sup>7</sup>. For the other LBL assembly partner, PVA was driven to SWNT adsorption surface by hydrogen

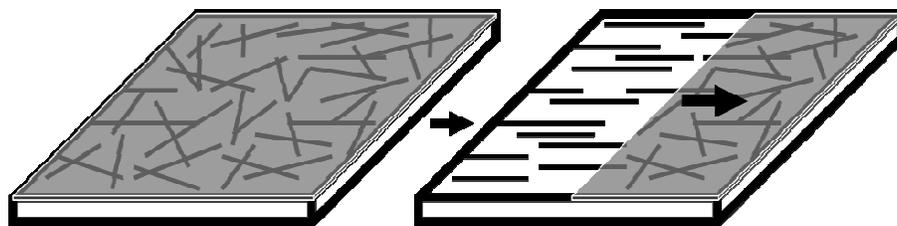
bonding, charge transfer, and hydrophobic interactions. Therefore, by alternately dipping a charged glass into the PVA solution and the SWNT dispersion, we can easily obtain almost single stranded dispersion quality of SWNTs in PVA matrix. (**Figure 1.**) The unique processing features of LBL assemblies include the direct transfer of SWNT dispersion level from solution state to solid state unlike other mixing and drying processes. Well exfoliated SWNTs in solution state adsorb onto the PVA surface without losing their dispersion quality during the simple dipping step. This direct adsorption solidifying step is critically contrasted with other conventional fabrication process.



**Figure 1.** Randomly oriented but well dispersed SWNTs in a SWNT-polymer LBL composite film. The bar represents 1  $\mu\text{m}$ .

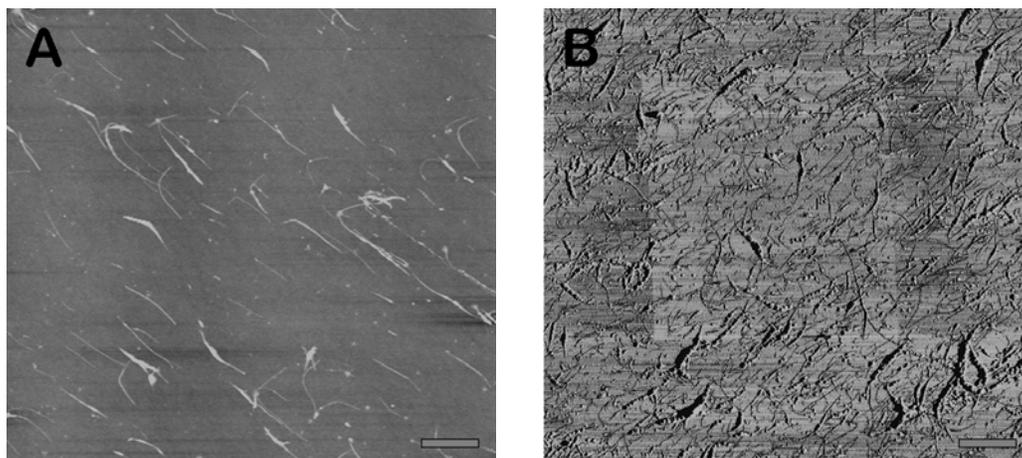
The main purpose of fabricating uniformly dispersed SWNT composites is to efficiently transfer the SWNT's superior nano-scale physical properties to macro-scale composites. Although the homogeneity may not be the only factor affecting the composite properties, we could achieve high electrical and mechanical properties at the same time mostly by improving the dispersion quality. For pristine SWNTs, the preliminary electrical conductivity and mechanical tensile strength for the LBL assembled composite become around  $7 \times 10^3 \text{ S/m}$  and 170 MPa respectively. For oxidized SWNTs, the tensile strength extended up to around 450MPa. We believe that those efficient SWNT reinforcements are the results of molecularly controlled homogeneous dispersion of SWNTs by hydrogen bonding directed LBL assemblies.

For improving the composite properties, the effective alignment of functional SWNTs in controlled directions are the next desirable steps. Here, we introduce that randomly oriented SWNTs were aligned by air-water interfacial forces through “SWNT combing” (**Figure 2**).



**Figure 2.** Schematic of SWNT combing process by air-water interfacial forces

Alignment of SWNTs was performed on a wet surface with randomly oriented SWNTs by the application of a high pressure air jet. Previously introduced DNA combing effect also produced similar alignment topography as SWNT combing<sup>8,9</sup>. However, the pressurized air flow over a wet surface improves the alignment efficiency by increasing the hydrodynamic force that is exerted on the cylindrical SWNTs, as opposed to DNA combing which utilizes natural water receding interaction. Atomic force microscopy (AFM) images show the aligned SWNTs from the SWNT combing method (Figure 3). The alignment efficiency is extremely high, with more than 80 % of the SWNTs aligned unidirectionally. These alignment effects were not only applied to the first layer but also successfully introduced to the subsequent layers (Figure 3 B). Therefore, we were able to fabricate a LBL multilayer of aligned SWNTs by a fusion technique of SWNT LBL assembly and SWNT combing.



**Figure 3.** Atomic force microscopy (AFM) images for (A) 1 layer of aligned SWNTs and (B) 2 layers of aligned SWNTs. (The scale bar represents 1  $\mu\text{m}$  each)

## CONCLUSION

In this communication, we introduced physical properties of uniformly dispersed SWNT composites and a new method to align SWNTs by utilizing air-water interfacial forces. This method can be successfully incorporated to LBL multilayer assemblies. The orientation of SWNTs was analyzed by AFM and polarized UV-vis spectroscopy. The alignment effects of SWNT combing were efficient enough to produce aligned SWNT-polymer composites, which still remain as an unexplored research field due to the lack of a robust fabrication method to produce aligned SWNT composites. Given the promising physical properties of LBL assembled SWNT composites, SWNT combing technique will further improve the functional anisotropy and material performances of SWNT LBL composites.

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