Title: Single Wall Carbon Nanotube Alignment Mechanisms for Non-Destructive Evaluation
Type of report: Final Report
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I. Introduction

The novel electric and mechanical properties of single wall carbon nanotubes (SWCNTs) allow one to envision a generation of new SWCNT-based functional devices such as ultra-light sensors and molecular electronic circuits [1]. For example, metallic SWCNTs have a very low resistance and can tolerate an extremely high current density. So, they can be ideal conducting wires for electronic circuits. Semiconducting SWCNTs can have various band gaps depending on their chiralities. These SWCNTs can be used for fabrication of SWCNT-based logic gates. Several researchers discovered that the conductivity of a SWCNT is very sensitive to chemical environments and mechanical deformation [2]. Now, one can even build versatile sensor components which can detect the change of chemical environments and mechanical stress applied on SWCNTs. Possible applications of SWCNT-based devices seem limitless.

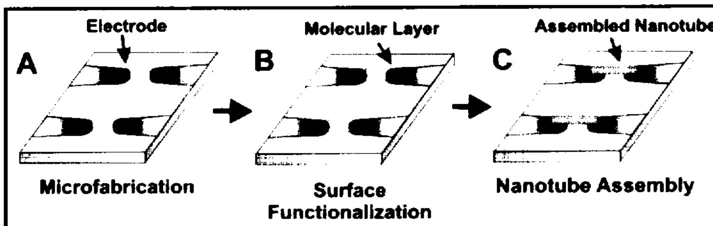

Figure 1. Schematic diagram depicting surface templated assembly process.

However, one still has to solve several challenging problems to achieve practical SWCNT-based devices. One of the major bottlenecks has been the lack of a fast fabrication tool. With SWCNT-based devices, individual SWCNTs work as a functional unit. Since individual SWCNTs are first synthesized in a powder form, nanometer scale assembly steps are required. Previous assembly methods include direct manipulation using micromanipulators [3], alignment via magnetic or electrostatic field [4], flow cell method [5], and assembly on e-beam generated patterns [6]. However, these methods are time-consuming and are not suitable for mass production of a large number of SWCNT-based devices.

Recently, we successfully applied *surface-templated assembly strategy* to assemble SWCNTs on solid substrates with precise *positioning* and *orientations* (Figure 1). In this strategy, solid surface is first functionalized with organic molecular patterns (Figure 1B) via direct deposition methods such as dip-pen nanolithography [7] and microcontact printing, and then the substrate is placed in the SWCNT solution so that SWCNTs assemble onto the molecular patterns due to electrostatic attractions (Figure 1C).

II. Significant Achievements

A) New Assembly Mechanism of Carbon Nanotubes on Solid Substrates.

The assembly process is based on a long range electrostatic interaction between substrate functional groups and carbon nanotubes in the solution [6]. During the assembly process, carbon nanotubes are attracted toward the surface charge on the molecular patterns, and they assemble onto the surface patterns in a configuration which minimizes the electrostatic potential energy. Thus, *the shapes of surface molecular patterns* determine the final configuration of assembled SWCNT structures. Figure 2

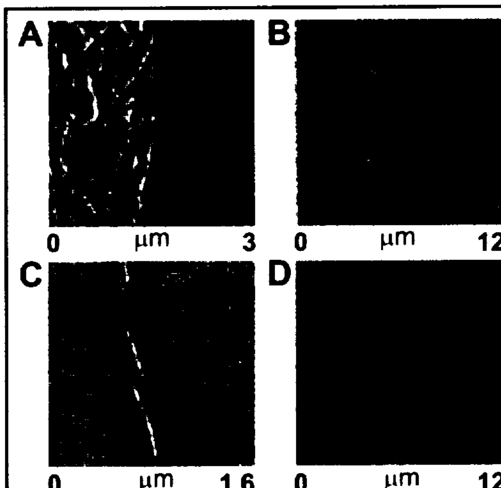

Figure 2. SWCNTs assembled onto cysteamine molecular patterns with various shapes. (A) and (B) SWCNT mesh on wide line patterns. (C) Multiple SWCNT lines on narrow lines. (D) Individual SWCNTs assembled on nanoscale patterns.

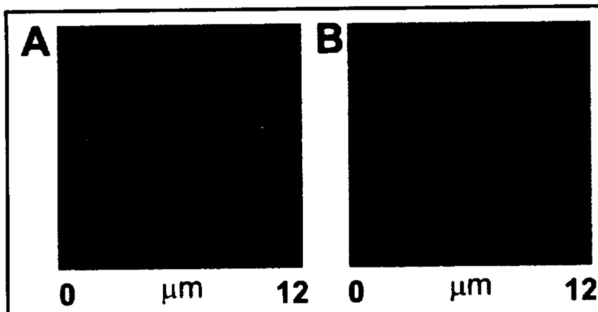

Figure 3. SWCNTs assembled onto cysteamine molecular patterns from (A) high concentration CNT solution and (B) low concentration CNT solution.

shows SWCNT structures assembled onto molecular patterns with various shapes. It clearly shows that the shapes of molecular patterns significantly affect the number of assembled SWCNTs as well as positions and orientations of final SWCNT structures. Significantly, utilizing proper surface patterns, one can even control the positions and orientations of *individual SWCNTs* (Figure 2D).

One key parameter for this process is the *assembly probability* of SWCNT onto the surface patterns. Various conditions affect the number of SWCNTs assembled onto the surface patterns. Figure 3 shows the effect of *SWCNT solution concentration*. When the molecular patterns are immersed in a high concentration SWCNT solution, multiple SWCNTs are attracted onto the surface patterns simultaneously, and the entire surface pattern area is covered by SWCNTs (Figure 3A). Surprisingly, we can assemble only a single SWCNT onto each molecular pattern utilizing a *low concentration* solution leaving wide empty area on the molecular patterns. This phenomenon has not been observed before, and the exact reason is still unknown. One possible explanation is a *screening effect*. At low concentration, the separation between individual SWCNTs in the solution is very large, and at any given moment, only a single SWCNT touches the surface patterns. In this case, once one SWCNT assembles onto the surface pattern, the assembled SWCNT screens out the electrical field from the surface molecular patterns and reduces the probability of second SWCNT assembly. This result has significant practical importance. It implies that one can now assemble and control individual SWCNTs utilizing *micrometer scale* molecular patterns. Since micrometer scale patterning can be done by fast conventional patterning methods such as microcontact printing or photolithography, one can finish the entire assembly process without relying on relatively slow serial nanofabrication processes. This is a unique feature of this new process which may open up the possibility of *fast mass production* of SWCNT-based integrated circuits.

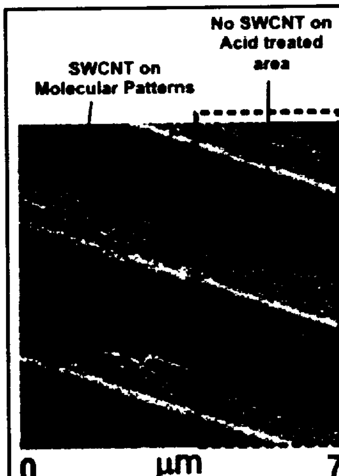

Figure 4. SWCNT assembly onto 4-mercaptopyridine molecular patterns *with* and *without* acid treatment.

One can also change the assembly probabilities by changing the charge density on the surface molecular patterns. Figure 4 shows the preliminary results. In the experiment, 4-mercaptoimidazole patterns are first created via the microcontact printing method. Then, the right half of the pattern is treated in the acid solution, which reduces the charge density in the 4-mercaptopyridine molecular patterns. As a result, no SWCNT assembles onto the acid-treated surface area even though it still shows clear molecular patterns. This implies that one can enhance or reduce the assembly probabilities by simple treatment of changing the charge density on the surface molecular patterns.

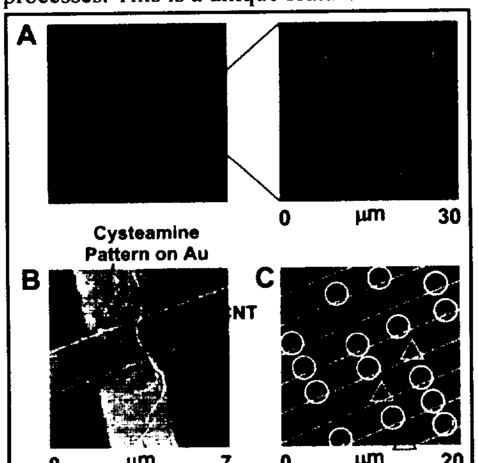

Figure 5. (A) SWCNT array on a flat Au surface. (B) Single SWCNT electrode structure. (C) Assembly results on multiple electrodes showing the current fabrication yield. Junctions with 0, 1, or 2 SWCNTs are marked by triangles, circles, or rectangles, respectively.

B) A Mass Production Method for Very Large Scale Integrated Circuits Based on Single Wall Carbon Nanotubes.

We, for the first time, demonstrated, that this strategy can be utilized to assemble a large number of individual SWCNTs on solid substrates with precise positioning and alignment (Figure 5A). In this experiment, *1cm* x *1cm* sample area is covered by individual SWCNT array. This can be one of the major breakthroughs in SWCNT and general nanowire-based applications because we now have an assembly tool as fast as conventional microfabricaion methods. We also demonstrated assembly of SWCNT mesh between microfabricated electrodes (Figure 5B and 5C). In Figure 5B, specific regions of Au electrodes are first functitonalized with cysteamine molecules. When the substrate is placed in the SWCNT solution, only a single SWCNT assembles between the electrodes on the desired location even though the pattern size is as large as a micrometer. When the same experiment is done on a large number of electrodes, we can build multiple electrical junctions with a single SWCNT (Figure 5C). The current fabrication yield on a flat surface is better than 90% (Figure 5A). On electrode structures, we can achieve about 70 % yield (Figure 5C), and it is rapidly rising. We can now envision a generation of new integrated SWCNT devices of vital importance to NASA. These include gas sensors, mechanical devices, and health monitoring devices.

C) Quick Testing Method for Single Wall Carbon Nanotube Based Electronic Components

The properties of the assembled SWCNT device structures can be tested by a conducting atomic force microscope (CAFM) (Figure 8). CAFM utilizes a conducting tip as a probe to measure the current between the tip and the electrode on the substrate. It allows us to obtain conductance maps of the SWCNT junctions. We already demonstrated that CAFM can be utilized to study electrical properties of SWCNTs on clean electrodes (Figure 8). This technique can be utilized to characterize various properties of SWCNT-based circuit components such as: 1) contact resistance, 2) resistance of assembled SWCNTs, and 3) the effect of adsorbed molecules on a SWCNT.

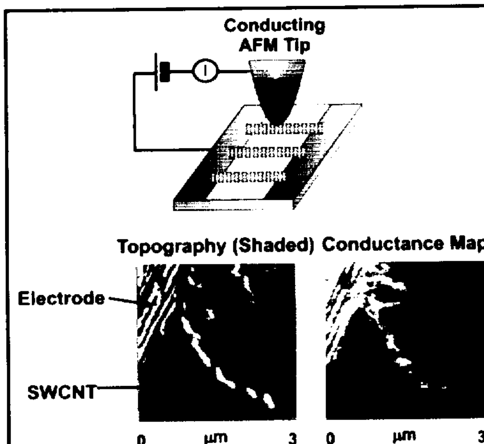

Figure 8. Conducting atomic force microscope data showing the resistance map of SWCNT on the electrode.

III. Summary

As proposed in our original proposal, we developed a new innovative method to assemble millions of single wall carbon nanotube based circuit components as fast as conventional microfabrication processes. This method is based on surface template assembly strategy. The new method solves one of the major bottlenecks in carbon nanotube based electrical applications and, potentially, may allow us to mass produce a large number of SWCNT-based integrated devices of critical interests to NASA.

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Abstract

As proposed in the original proposal, we developed an innovative method to assemble extremely large number of electronic circuit components based on individual single wall carbon nanotubes (SWCNTs) as fast as conventional microfabrication processes. The method is based on a surface templated assembly strategy where the surface of the solid substrate is first functionalized with self-assembled monolayer molecules via dip-pen nanolithography and microcontact printing, and the assembly of SWCNTs is directed onto the molecular patterns via specific interactions between surface functional groups and SWCNTs in the solution. Utilizing this method, we were able to cover a large substrate area ($1cm^2$) with millions of SWCNT-based circuit components in a short time period. This result removes one of the major bottlenecks in SWCNT-based electronic applications and allows us to envision integrated SWCNT-based devices.

REPORT OF INVENTIONS AND SUBCONTRACTS
(Pursuant to "Patent Rights" Contract Clause) (See Instructions on Reverse Side.)

FORM APPROVED
OMB NO. 0704-0016

1a. NAME OF CONTRACTOR/SUBCONTRACTOR	c. CONTRACT NUMBER	2a. NAME OF GOVERNMENT PRIME CONTRACTOR	c. CONTRACT NUMBER	3. TYPE OF REPORT *(check one)*
Florida State University	NAG-1-02022			☐ INTERIM ☒ FINAL
b. ADDRESS *(include Zip Code)* 118 N WOODWARD AVE, TALLAHASSEE, FL 32306-4166	d. AWARD DATE *(YYMMDD)* 02/03/07	b. ADDRESS *(include Zip Code)*	d. AWARD DATE *(YYMMDD)*	4. REPORTING PERIOD *(YYMMDD)* FROM: 02/03/07 TO: 02/12/16

SECTION I - SUBJECT INVENTIONS

5. "SUBJECT INVENTIONS" REQUIRED TO BE REPORTED BY CONTRACTOR/SUBCONTRACTOR *(If "None", so state)*

a. NAME OF INVENTOR(S) (Last, First, M.I.)	b. TITLE OF INVENTION(S)	c. DISCLOSURE NO., PATENT APPLICATION SERIAL NO. OR PATENT NO.	d. ELECTION TO FILE PATENT APPLICATIONS: UNITED STATES YES	UNITED STATES NO	FOREIGN YES	FOREIGN NO	e. CONFIRMATORY INSTRUMENT OR ASSIGNMENT FORWARDED TO CONTRACTING OFFICER: YES	NO
Seunghun Hong Saleem G. Rao Ling Huang	POSITIONING WIRES ON A SURFACE 3/10/2003 Dr. Seunghun Hong, PI	PROVISIONAL PATENT APPLICATION NO.: 064560-2002						

f. EMPLOYER OF INVENTOR(S) NOT EMPLOYED BY CONTRACTOR/SUBCONTRACTOR.

i. NAME OF INVENTOR *(Last, First, M.I.)*	i. NAME OF INVENTOR *(Last, First, M.I.)*
ii. NAME OF EMPLOYER	ii. NAME OF EMPLOYER
iii. ADDRESS OF EMPLOYER *(include Zip Code)*	iii. ADDRESS OF EMPLOYER *(include Zip Code)*

g. ELECTED FOREIGN COUNTRIES IN WHICH A PATENT APPLICATION WILL BE FILED.

i. TITLE OF INVENTION	ii. FOREIGN COUNTRIES OF PATENT APPLICATION

SECTION II - SUBCONTRACTS *(Containing a "Patent Rights" clause)*

6. SUBCONTRACTS AWARDED BY CONTRACTOR/SUBCONTRACTOR. *(If "None", so state)*

a. NAME OF SUBCONTRACTOR(S)	b. ADDRESS *(include Zip Code)*	c. SUBCONTRACT NO. (S)	d. DAR "PATENT RIGHTS" CLAUSE NO.	DATE *(YYMM)*	e. DESCRIPTION OF WORK TO BE PERFORMED UNDER SUBCONTRACTOR(S)	f. SUBCONTRACT DATES *(YYMMDD)* AWARD	ESTIMATED COMPLETION
None							

SECTION III - CERTIFICATION

7. CERTIFICATION OF REPORT BY CONTRACTOR/SUBCONTRACTOR. *(Not required if* ☐ *Small Business or* ☒ *Non-Profit organization.) (Check appropriate box)*

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Raymond E. Bye Jr.
3-12-03

b. TITLE
Vice President for Research, FSU

c. I certify that the reporting party has procedures for prompt identification and timely disclosure of "Subject Inventions," that such procedures have been followed and that all "Subject Inventions" have been reported.

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