

Self-Assembled, Deterministic Carbon Nanotube Wiring Networks**

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One promise of molecular electronics is that it is potentially amenable to a “bottom-up”, self-assembly-based manufacturing approach. This would provide an interesting alternative for circuit fabrication when devices are scaled to a few tens of nanometers in size and smaller.^[1] However, major challenges exist in developing architectures suitable to bottom-up fabrication, as well as in devising the circuit fabrication techniques themselves. For example, self-assembly leads most readily to periodic structures,^[2] and, while the starting materials for such approaches may be highly purified, the assembly steps themselves are unlikely to be perfect. Furthermore, various structural parameters of a circuit that are obtained through lithographic patterning, such as the length, diameter, orientation, and separation (pitch) of the wires, can be substantially more difficult to control by using chemical assembly. Finally, nanowires with the most desirable electrical characteristics, such as single-walled carbon nanotubes (SWNTs), do not necessarily have the chemical properties required for controlled self-assembly.

Four years ago, one of us reported on the relevance of the crossbar circuit for molecular electronics.^[3] From the perspective of bottom-up assembly, the crossbar is attractive because it is simple, ordered, and defect-tolerant, and it may be utilized for both memory and logic. Here we present a room-temperature, “minimal-lithography” technique for chemically assembling small deterministic crossbars of SWNT ropes. The length of the SWNT ropes is varied from 1 to 20 μm by a solution-phase, chemically controlled aggregation of much shorter ($\approx 0.5 \mu\text{m}$) SWNTs. The orientation and spatial positioning of the SWNTs are induced by an alternating current (AC) electric field. The pitch of the nanotubes within the crossbar is controlled between 100 nm and 2 μm , essentially as a result of the chemical control of the screened Coulombic interactions between the (electrically charged) SWNTs. The electrical charge on the SWNTs is qualitatively

determined by solvent–SWNT interactions. Consequently, all of the critical structural parameters of the crossbars were controlled without lithographic assistance. Low-resolution patterning of the electrodes that generate the AC field was the only lithographic step required. We also report on a theory of the crossbar fabrication, which identifies the important chemical variables for manipulating this self-assembly process. Transport measurements through crossbar assemblies are reported as a consistency check against literature measurements for randomly assembled crossed-SWNT structures.

The excellent conductivity properties of SWNTs make them ideal wiring candidates for molecular-scale circuitry. Dai's group has developed wafer-based growth procedures that can generate aligned SWNTs.^[4] However, this technique requires lithographic definition of SWNT nucleation sites, as well as high-temperature processing—neither of which is compatible with molecular-based nanoscale architectures. Lieber's group has recently reported on a nanowire crossbar fabrication approach that employs microfluidics to align semiconductor nanowires within lithographically defined channels, coupled with deposition onto a chemically patterned surface.^[5] That approach worked under ambient conditions, and certain parameters, such as nanowire length and diameter, were chemically controlled. However, lithographic definition of some of the critical aspects of the crossbar, such as nanowire pitch and orientation, was required. SWNTs are flexible, have limited solubility, and techniques to control properties such as nanotube length and aggregation have not been well developed. Consequently, most SWNT devices to date have relied on effectively random single-device assembly events, such as the fortuitous crossing of two tubes to produce a single junction.

The controlled aggregation of SWNTs to form ropes, without precipitating the nanotubes, turned out to be critical for ultimately controlling our crossbar structures. Solubilization of SWNTs typically requires the use of surfactants^[6] or polymer wrapping.^[7] However, we have been able to disperse HipCO tubes (HipCO = high pressure carbon monoxide) in *ortho*-dichlorobenzene (ODCB) in relatively high concentrations ($\approx 0.01\%$ by weight) with minimal sonication times (≈ 10 min). SWNTs produced by the recently developed HipCO (high pressure carbon monoxide) process^[8] tend to have smaller diameters than SWNTs produced by laser ablation. Atomic force microscopy (AFM) characterization confirms that the dispersed tubes are isolated single strands and/or small ropes, with diameters ranging from 0.8 to 1.3 nm, and lengths from 0.1 to 1.5 μm , with the majority of the tubes being shorter than 0.5 μm . Electroplating experiments revealed that the SWNTs in ODCB are positively charged—a result that we attribute to the large electron affinity of ODCB. By contrast, when SWNTs are suspended using certain nonionic surfactants,^[9] colloids of negatively charged SWNTs are produced. We achieved controllable aggregation of the SWNTs by diluting a SWNT/ODCB solution with CHCl_3 . A typical solution is prepared by diluting 1.5 mL of a SWNT/ODCB solution ($10^{-4}\%$ of SWNT by weight) in 250 mL of CHCl_3 while sonicating. Such a solution led to SWNT ropes of diameters between 6 and 20 nm and lengths ranging from 1 to

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20 μm , with longer ropes having larger diameters. A lower weight percent of SWNTs led to shorter ropes, while a higher weight percent led to longer ropes. Electroplating experiments indicated that the SWNTs retained their charge after addition of CHCl_3 . CHCl_3 and ODCB have similar dielectric constants. Other solvents that were co-miscible with ODCB but that were a poor dielectric match, such as hexane, caused complete precipitation of the SWNTs.

Electric field assisted deposition and orientation of the nanowires^[10, 11] was accomplished by patterning two parallel electrodes with a 10 μm gap onto a silicon wafer coated with 0.5 μm SiO_2 .^[12] This device was immersed in a suspension of SWNTs dispersed in a solution that contained 0.4 mL of ODCB and 100 mL of CHCl_3 . An AC field was generated by applying a 20 $\text{V}_{\text{p-p}}$ AC voltage at 4 MHz for a period of 4 to 15 minutes while the solution was stirred. After deposition, the electrode was chemically etched away, and a new electrode set was deposited perpendicular to the first set. Then, the SWNT deposition was repeated. Previous authors have demonstrated that various nanowires, including SWNTs, when deposited onto a surface, will withstand simple device processing steps.^[13a-c] We also found this to be the case.^[12] The electrical character of the assembled crossbars was tested by using electron beam lithography to pattern electrode connections onto several of the SWNTs in a given crossbar.^[13]

Three SWNT crossbars of varying structural characteristics are shown in Figure 1. A key result of this work is that the pitch of the crossbar was controllable and correlated with the length of the SWNT ropes. As the width of the length distribution of the SWNT ropes increased, the fluctuations in crossbar pitch also increased (Figure 2).

We have developed a model of this assembly process to understand the various chemical and physical parameters that can be used to control crossbar formation. The fact that a characteristic length scale (the pitch) arises during the crossbar fabrication process is the result of inter-SWNT rope repulsive interactions that are strongly screened by the solvent and the ODCB counterions, as suggested by the experimental observation that the solvated ropes are positively charged. The constrained geometry of the electrodes also plays an important role. Because of the field-generated alignment force, the deposition of the ropes is effectively confined to a single dimension and a local area—that is, perpendicular to the electrode stripes and within the area between the two electrodes.^[14] The first ropes to arrive deposit parallel to each other (aligned to the field) at random positions on the electrode and, once deposited, they remain in their positions due to large van der Waals interactions with the substrate. However, as the density of deposited ropes increases, the electric field in their vicinity is modified by their presence. An incoming rope will then fall at the point of lowest repulsion from its neighboring ropes; for example, equidistant between ropes of equal length. During this process, a point will be reached at which tube repulsion will balance the driving force to deposition, resulting in a critical inter-rope distance or pitch (p).

This critical condition may be understood from the local energetics of the problem: the screened interaction (repulsive) energy of the incoming rope with the already deposited

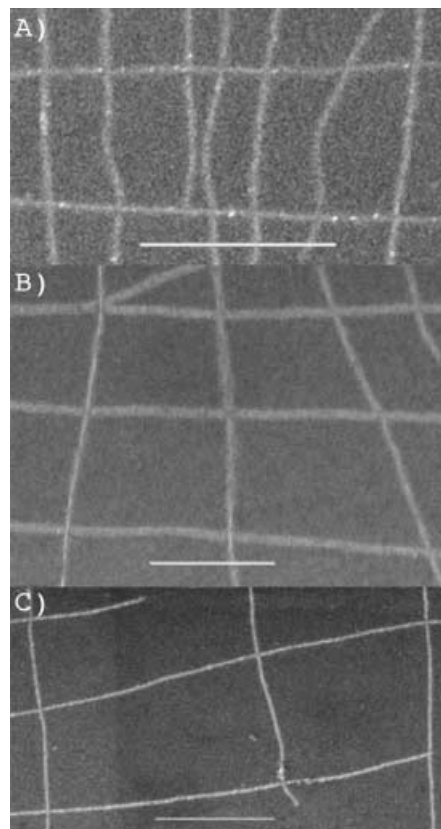


Figure 1. Scanning electron micrographs of SWNT crossbars with varying pitch. Scale bars are 500 nm for a) and b), and 1 μm for c). The diameter of the ropes is not well measured with this technique, but can be measured with force microscopy. The shortest (500 nm) wires are characterized by diameters of 1–2 nm, while the longest (20 μm) wires possess diameters ranging from 10 to 15 nm. SWNT rope lengths [μm]: a) 3.7 ± 0.3 & 1.2 ± 0.33 ; b) 2.8 ± 0.53 ; c) 3.8 ± 1.2 .

ropes is balanced against its Coulomb and polarization energies under the external field. In fact, the Coulomb energy is the dominant contribution in the experimental conditions considered here. We believe that a thin charged rod will capture the main features of the electrostatic processes of the SWNTs involved. Although their transport properties ensue from their quantum nature, nanotubes behave as classical objects in many other respects. In particular, *ab initio* calculations^[15] have shown that the screening of applied electric fields by nanotubes is remarkably similar to that of cylindrical conductors with equivalent aspect ratio.^[16]

To obtain the electrostatic potential of the deposited tubes in the presence of surrounding counterions (ODCB) in a solvent with a dielectric constant ϵ (CHCl_3), we use the linearized Poisson-Boltzmann (PB) equation.^[12] The key aspect of the solvation process is the appearance of a characteristic screening length $1/\kappa$ given by equation (1),

$$\kappa^2 = \frac{4\pi(qe)^2}{\epsilon k_B T} \rho_c \quad (1)$$

where e is the fundamental unit of charge, qe the counterion charge, T the temperature, k_B the Boltzmann constant, and ρ_c the ionic ODCB density. The ropes have a large aspect ratio, so they can be characterized by λ , which is their line charge density per unit length. Thus, ρ_c may be estimated from the

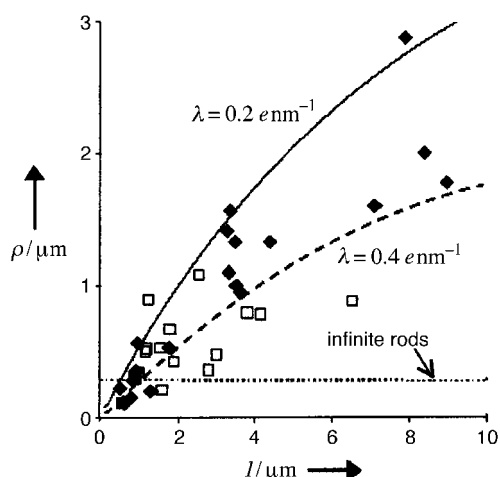


Figure 2. The pitch $[p/\mu\text{m}]$ versus the rope length $[l/\mu\text{m}]$, calculated for two linear charge densities $[\lambda/e\text{nm}^{-1}]$ and for $\rho_t = 4 \times 10^9$ tubes per mL in a HCCl_3 solution with ODCB counterions. Experimental data, plotted as black diamonds and open squares, represents crossbars formed from tubes that were characterized by similar lengths to within 25% and 50%, respectively. In spite of their large aspect ratios, the ropes interact with each other more like finite charges rather than infinite rods, at regimes determined by $\kappa l \sim 1$. This condition holds except for the shortest ropes ($l < 2 \mu\text{m}$), in which case the screening lengths overlap strongly and so the approximations used in the model are no longer valid. For comparison, the solution obtained from infinite rods is also plotted. For that case, there is no length dependence, but the limiting behaviors show that it is not the absolute length that makes a rod behave as “infinite” but rather its values κl and κr . Note that the charge density λ does not necessarily correspond to its experimental counterpart, as the theory requires λ to be suitably renormalized.

condition of overall charge neutrality $q\rho_c = \lambda < l > \rho_t$, where ρ_t is the number density of tubes in solution^[12] and $\langle l \rangle$ is the average tube length.

The screening length $1/\kappa$ not only determines the attenuation of the inter-rope repulsion, but, significantly, it establishes the interplay of length scales involved in this problem. In particular, it discriminates among the different asymptotic regimes of the potential. At one extreme,^[17] rods of length l separated by distances $r \ll l$ with $\kappa l \gg 1$ behave as infinite rods. Their potential can be described by the Bessel function of order zero. At the other extreme,^[18] rods with length $l \ll r$ and $\kappa l \sim 1$ behave as equivalent point charges of magnitude λl , as described by the Yukawa potential. The experimental conditions ($\kappa \sim 1 \mu\text{m}^{-1}$, $l \sim 1 \mu\text{m}$, so $\kappa l \sim 1$, $r \sim l$) fall in the intermediate regime but closer to the point charge regime. Hence, we use the more appropriate Yukawa potential (per unit length) $\phi = \frac{\lambda \exp(-\kappa r)}{\epsilon r}$ to obtain the energy. This yields the critical relationship of pitch (p) with SWNT rope length (l) [Eq. (2)], where E is the electric field and $\alpha = \alpha(l)$ is the polarizability; we have assumed ropes of equal length.

$$U(p/2) = \left(\frac{2\lambda l \exp(-\kappa p/2)}{p/2} - V_{\text{ext}} \right) \frac{\lambda l}{\epsilon} - \frac{\alpha E^2}{2} = 0 \quad (2)$$

We also assumed ODCB counterions with charge $-e$, although there is no qualitative difference for smaller values. In Figure 2 we compare some numerical solutions of this equation to the experimental data. Consistent with our assumptions, the agreement is better when the deposited

SWNT ropes are of nearly equal length. The model also underscores the importance of correctly describing the solvation process: both the screened and bare infinite rod limits fail to reproduce the experiments. These results imply that experimental control over the SWNT length is a critical chemical handle for manipulating crossbar formation: longer ropes with higher polarizability should lead to a decrease in the pitch. This should be complemented by an optimization of the interplay between polarizability and the properties of the applied voltage.^[14]

These crossbars are not meant to serve as models for interrogating transport physics through nanotubes. Nevertheless, simple transport experiments can address whether the junctions actually conduct, and whether or not the assembly technique, which bears some similarities to electrophoretic separation approaches,^[14] might be selective for tube type, although it is unlikely that such selectivity would be important at frequencies as low as 4 MHz. Using standard e-beam lithography procedures, we wired up and interrogated the electrical character of a number of aligned SWNT ropes and found that the ropes were, in fact, a statistical mix of metals and semiconductors.^[12] The current–voltage characteristics of a single SWNT rope, and for a crossed junction containing that rope, are presented in Figure 3. This particular junction is

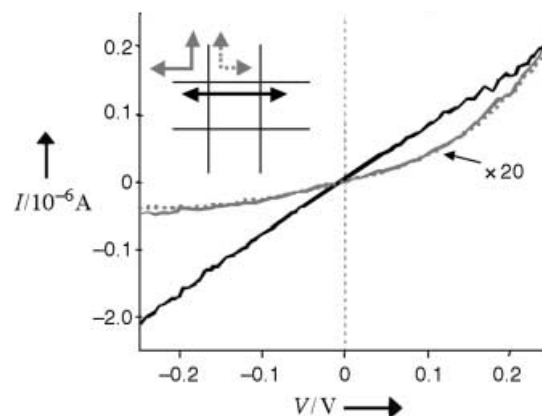


Figure 3. Transport through a single wire (black curve) and through a crossed junction (dotted curve) of a nine-junction nanotube crossbar structure.

diode, perhaps resulting from a metallic rope crossing a semiconducting rope.^[19] Both diodic and ohmic responses were observed for other junctions. These results indicate that the junctions are reasonably conducting, although the current through our devices is relatively low,^[12, 19, 20] perhaps because of contact resistance. The devices could be annealed at elevated temperatures, which resulted in higher conductivity. However, for our particular applications, thermal annealing must be balanced against the requirements for incorporating molecules into the nanotube junctions, and so we report only unannealed devices here.

Our results indicate that it is possible to fabricate deterministic wiring networks from SWNTs by using chemical self-assembly. While this process is currently limited to the fabrication of relatively small (4×4 and less) crossbars, our

simple model indicates that the optimization of several experimental handles may lead to the assembly of large-scale structures. For example, maximizing the length and mono-dispersity of the SWNT ropes, as well as controlling dielectric screening and SWNT charge density, are all identified as key handles for improving this process. Furthermore, the frequency of the orienting AC field represents a variable that has not yet been optimized. We found little frequency dependence to this process between 10^4 Hz and 10^6 Hz. This is likely because the intertube Coulomb repulsions are dominant in this regime. However, at much higher frequencies, our calculations suggest that the polarizability of the tubes should become important, at which point the circuit pitch may decrease as it approaches the limit for infinite rods (Figure 2). We are currently designing experiments at $>10^9$ Hz deposition frequencies to explore this effect. We remark that none of these experimental handles to circuit fabrication require the use of lithographic techniques. Thus, relatively inexpensive routes toward fabricating designed circuits with characteristic dimensions on the order of a few nanometers may be possible.

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Protein Affinity Labeling Mediated by Genetically Encoded Peptide Tags**

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Affinity labeling is a powerful method by which protein residues in the immediate vicinity of a labeled ligand can be identified. Most such experiments employ latently photo-activatable groups such as benzophenones^[1] or azides^[2] attached covalently to a ligand of interest. When photolyzed, the resultant intermediate inserts into a carbon–hydrogen bond of the protein which results in the covalent coupling of the molecule of interest with its receptor. These experiments generally have been employed to identify active site residues proximal to the site of ligand or substrate binding.^[3, 4]

Traditional affinity-labeling techniques have limitations when the ligand of interest is a protein and the goal is to identify the binding partners of that protein. With the exception of small proteins that contain only a single nucleophilic cysteine,^[5] it is difficult to produce site-specifically labeled proteins by standard conjugation chemistry. An appealing solution to this problem would be to develop a genetically encoded peptide tag capable of binding an affinity-labeling reagent with high specificity. We demonstrate here that the complex of Ni^{II} with the tripeptide NH₂-glycine-

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