**Controlled formation of carbon nanotube junctions via linker induced assembly in aqueous solution**

Matteo Palma*, Wei Wang, Erika Penzo, Julian Brathwaite, Ming Zheng, James Hone, Colin Nuckolls and Shalom J. Wind*


Polymers Division, National Institute of Standards in Technology, 100 Bureau Drive, Gaithersburg, Maryland 20899-8542, United States

RECEIVED DATE (automatically inserted by publisher) E-mail: mp2766@columbia.edu; sw2128@columbia.edu

Supporting Information Placeholder

**ABSTRACT:** Here we describe a simple approach for the controlled formation of one-dimensional and multi-terminal nanotube junctions. We describe a facile bottom-up strategy for joining the ends of single walled carbon nanotubes. The geometry of the junctions can be varied and controlled by linker induced assembly of DNA wrapped nanotubes.

Here we present a simple bottom-up approach for the controlled formation of end-to-end single walled carbon nanotube (SWCNT) junctions via directed chemical reactions. CNT based nanoscale devices require junctions among different nanotubes, as well as between CNTs and functional molecules/moieties. In particular, junctions obtained from SWCNTs are of interest for nanoscale electronic devices because of the nanoscale diameter of the tubes and their room temperature transport properties. SWCNT/SWCNT junctions have been observed in samples produced with different techniques, such as chemical vapor deposition (CVD), laser ablation, and electrical welding. Additionally, multi-terminal SWCNT junctions have been irregularly produced by arc discharge methods, laser ablation techniques, CVD processes, and electron-beam welding. Ring-like CNTs have also been synthesized by several methods, such as covalent ring-closure reaction, noncovalent interactions, floating CVD method, and electron beam irradiation.

CNTs have been further interconnected via chemical functionalization in solution, but without effective control over the junction formation (end-to-end and/or end-to-side). Recent studies by Swager and coworkers produced SWCNTs terminally linked by oligonucleotides into a nanowire motif, employing a side-wall protection step to overcome regiospecific SWCNT covalent attachment.

In the study presented here we direct chemical reactions at the ends of well-defined segments of SWCNTs to form junctions of end-to-end linked tubes. We further find that different shaped linkers yield SWCNTs with higher order structures that go beyond simple linear arrays to ones that are multiterminal and circular. These unusual structures are formed from a self-assembly process in aqueous solutions that is controlled by the geometry, and the chemical nature, of the linker.

The SWCNTs used in this study, were sonicated and dispersed in water via side-wall interactions with single-stranded DNA (see supporting information). DNA-assisted dispersion of SWCNTs enables nanotube separation by chirality and electronic structure (i.e. metallic vs semiconducting). The helical wrapping of the SWCNT with DNA further allows the separation of nanotubes by length via size-exclusion chromatography. Moreover, this method leaves only the terminal ends of the SWCNTs available for direct functionalization.

SWCNTs sonicated in water exhibit functional groups due to the use of ultrasound when preparing the suspension. ‘H atoms and ‘OH radicals are in fact generated upon sonication in aqueous solutions and can then either combine to form H₂, H₂O₂ (and water), or attack solute molecules, which can therefore be oxidized. The presence of carboxylic acid groups on the terminal ends of our nanotubes is further supported by the observed immobilization of activated nanotubes on amine functionalized (nano)patterns: see supporting material and figure SI-1. We exploit this selectivity to link SWCNTs in amidation reactions with amino-
functionalized molecular linkers forming only end-to-end junctions.

Figure 1 depicts the three different linkers used for this purpose (labeled A, B and C). Varying the type of linker allows us to create either linear (A) or multi-terminal (B,C) SWCNT junctions, where the geometry of the junction is dictated by the chemical and geometrical nature of the molecular linker.

Figure 1. The three different molecular linkers employed: A) Hexamethylenediamine, B) Polypropylenimine tetramine dendrimer, and C) PAMAM dendrimer, ethylenediamine core.

SWCNT carboxylic acid end-groups were activated in buffer solutions containing standard amide coupling and activating agents (Sulfo-NHS and EDCI)\(^3\); see supporting material for the experimental details. This chemistry covalently connects the amine-functionalized molecules to the end of the nanotubes, via an amidation reaction. Employing diamine molecular bridges, we were able to link different SWCNT segments via a simple reaction strategy in environmentally friendly aqueous solutions. The molecular linkers employed presented multiple amine functionalities in order to bridge two, or more, SWCNTs.

To determine the degree of coupling and to monitor the self-assembly, we cast low coverage films on silicon wafer substrates and imaged them with atomic force microscopy (AFM) and transmission electron microscopy (TEM). The starting SWCNTs before reaction have an average length of 147.7 ± 92.8 nm (see figure 2a and 2b).

Figure 2. a) AFM topographical image of pristine DNA wrapped SWCNTs and schematic of a DNA wrapped CNT; b) Normalized histogram of pristine DNA wrapped SWCNTs length distribution: average length (147.7 ± 92.8) nm as determined from ca 900 SWCNTs.

Fig 3 shows AFM and TEM images of linear SWCNT junctions typically obtained employing molecule A as a linker. The average length of SWCNTs segments was found to increase from (147.7 ± 92.8) nm for the pristine DNA-wrapped SWCNTs (starting material, see histogram in figure 2b), to (418.2 ± 370.1) nm when linear molecule A was allowed to react with (i.e. bridge) SWCNTs in solution (see figure 3c). This significant increase in average lengths of the SWCNTs visualized on the substrate surface indicates the formation of linear SWCNT junctions (see also figure SI-2 and SI-3).\(^{36,37}\)
**Figure 3.** Schematic of linear end-to-end SWCNT junctions; a) AFM topographical image and b) TEM image, of linear end-to-end SWCNT junctions formed employing molecular linker A; c) normalized histogram of the length distribution of the observed linear junctions: average length (418.2 ± 370.1) nm, as determined from ca 200 nanotube junctions.

In order to create multi-terminal SWCNT junctions we employed branched molecular bridges and interconnected pristine SWCNTs via the same functionalization strategy (i.e. amidation) described above. Figures 4a and 4b show various multi-terminal SWCNT junctions formed employing linker B (see also fig SI-4). These Y-junctions predominantly exhibit the same height of the pristine SWCNTs (i.e. around 1.2 nm): thus the junctions are the result of nanotube interconnections. The tubes in these junctions exhibit an average length of (522.5 ± 351.4) nm (see histogram in figure 4c). Notably, junctions, such as the ones produced, are of interest for the creation of three terminal nanotransistors.

**Figure 4.** Schematic of a Y-shaped end-to-end SWCNT junction; a) TEM image and b) AFM topographical image of multibranched end-to-end SWCNT junctions formed employing molecular linker B; c) normalized histogram of the length distribution of the observed B-linked SWCNTs: average length (522.5 ± 351.4) nm, as determined from ca 200 nanotube junctions.

We further employed molecule C as a molecular bridge in SWCNT junction formation. The longer branched chains minimize steric hindrance effects upon amidation of two or more SWCNTs; furthermore the amide functional groups can induce hydrogen-bond formation among different molecules/linkers, and therefore add an extra noncovalent stabilizing effect. Figure 5a shows a TEM image of the typical multi-terminal junctions observed employing linker C (see also figure SI-5). The average length of such junctions was determined to be (524.1 ± 366.9) nm, as shown in the histogram in figure 5b.

Employing molecular bridge C we found evidence of side-to-side interactions among multiple SWCNT's (see figure 6a). We also observed ring-like assemblies from the same solutions: figure 6b depicts such case (see also figure SI-6). Parallel nanotube arrays, can be useful for high-performance electronics applications, and there is indeed an interest in inducing such kind of assemblies. Moreover, ring-like structures can be potentially valuable as quantum interferometers for the production of tunable nanoscale electronic switching devices.

**Figure 5** Schematic of a Y-shaped end-to-end SWCNT junction; a) TEM image of multibranched end-to-end SWCNT junctions formed employing molecular linker C; b) normalized histogram of the length distribution for the observed C-linked SWCNTs: average length (524.1 ± 366.9) nm, as determined from ca 200 nanotube junctions.

The SWNTs assemblies we observed employing molecular bridge C (see figure 6) are likely to be stabilized by an interplay between van der Waals interactions and hydrogen bond formation among linkers bridging the nanotubes. Of note, trifluoroacetic acid (TFA) was added to SWCNT solutions to disrupt hydrogen bond formation among molecular linkers C belonging to different SWCNT junctions, and indeed no linear nor circular side-to-side assemblies were observed from TFA-treated solutions.

In summary, we have presented a facile and green strategy to fabricate linear and multi-terminal carbon nanotube junc-
tions using end-to-end linking of SWCNTs and subsequent linker-induced assembly. Furthermore, non-covalent interactions between molecular bridges have shown to allow for the formation of parallel and ring-like SWCNT assemblies. The approach presented is of general applicability for the sustainable fabrication of solution-processable CNT-based nanoscale devices. Three terminal connections to molecules can be used, for example, for the development of individually gated molecular logic devices. Moreover, the strategy presented here can be utilized to selectively dope (and therefore increase the conductivity) of semiconductor SWCNT networks, employing functional groups that can act as electron donors/acceptors.

Figure 6. SWCNTs assemblies employing molecule C as linker: (a) schematic and TEM image of parallel SWCNTs architectures and (as red dashes) the possible van der waals and hydrogen-bond interactions (among C linkers) involved in their formation; (b) schematic and AFM topographical image of circular SWCNTs assemblies: the average diameter of the observed ring-like architectures was found to be (408.1 ± 100.2) nm.

ACKNOWLEDGMENT

We gratefully acknowledge financial support from the Office of Naval Research under Award N00014-09-1-1117. Additional support from the Nanoscale Science and Engineering Initiative of the National Science Foundation under NSF Award CHE-0641523 and from the New York State Office of Science, Technology, and Academic Research (NYSTAR) is also gratefully acknowledged.
In order to verify that an amidation reaction and not a supramolecular interaction is actually responsible for the formation of SWCNT junctions, we have measured the length of SWCNTs after addition of the diamine molecular linker/s without the amide coupling and activating agents (Sulfo-NHS and EDCI). The results show that the average nanotubes’ length in this case is comparable to the length of pristine SWCNTs, thus indicating that the amidation reaction is the main driving force towards the formation of SWCNT junctions (see supporting material and figure SI-3 for a more detailed discussion).

The presence of unreacted species cannot be excluded; even after reaction we do see nanotubes that exhibit lengths comparable to single pristine tubes as evident by the nanotubes’ length distribution in the histograms of figure 3.

Bubble formation might also be involved in inducing the assembly of SWCNTs into circular architectures, and cannot be excluded a priori (see reference 18).