Directed assembly of one-dimensional functional nanostructures

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One-dimensional (1D) nanostructures have unique electronic, optical and mechanical properties that have attracted intense interest over the past two decades. Single wall carbon nanotubes (SWNTs) and semiconducting nanorods, in particular, have long been recognized as potential candidates for future nanoelectronic applications. 1D DNA nanostructures offer biofunctionality and are presently being explored for use as scaffolds and transport agents for both biological and inorganic nanospecies. Thus far, it has proven exceedingly challenging to take full advantage of the properties of these nanostructures. Their small size and the fact that their synthesis occurs either at high temperatures or in solution make it difficult to organize them in complex architectures, a key requirement for their exploitation. As a step toward this goal, we are developing an approach toward the controlled and ordered arrangement of 1D nanoobjects on lithographically patterned, chemically (or biochemically) functionalized surfaces. In this approach, a "breadboard" consisting of metallic nanodots is patterned by nanoimprint lithography and self-aligned pattern transfer [1]. These nanodots serve as anchors for the chemical or biochemical assembly of 1D nanostructures by selective functionalization with single stranded DNA (ssDNA) or other chemical moieties. Rigid DNA motifs and SWNT segments are attached to the dots, respectively, via DNA hybridization or through a covalent bond (Fig. 1).

We designed a double-crossover DNA motif composed of two anti-parallel DNA duplexes, connected by five crossover points (DFX). The DFX is ~ 4 nm wide and 60 nm long, well under the persistence length of ~ 100 nm and sufficiently rigid that it may be regarded as a 1D nanorod. Nanodot anchors, ~ 4 - 5 nm in diameter (Fig. 2), were patterned in arrays of dimers with an inter-dot spacing of 60 nm, matching the designed length of the DFX molecule. They were functionalized with ssDNA strands complementary to those found on the ends of the DFX, so that binding takes place by DNA hybridization. We studied the binding efficiency as a function of interaction strength by varying the length of the ssDNA linker. We found the overall yield of DFX bridging the nanodots to be close to 100%, independent of linker length; however the number of dimers bridged by a single DFX decreased while the rate of monomeric binding increased with the number of bases in the linker (Fig. 3).

Using the same basic approach, we have begun studying the selective binding of carbon nanotubes to the nanodot anchors. Fixed-length SWNT segments, wrapped with ssDNA [2] and cut by sonication in water [3], with an average length of 200 nm, were attached to amine-functionalized nanodot anchors arranged in a square lattice with a 200 nm pitch. Binding occurs via an amide bond formed by a reaction between the amines on the dots and carboxyl groups formed at the ends of the SWNT segments. The ssDNA wrapping prevents SWNT aggregation but does not inhibit the reaction of the carboxyl groups with the amines on the dots. The binding occurs preferentially at the ends of the tubes, and the yield is high (Fig. 4), with only 12 nanodots out of 223 having no SWNT segments attached.

The combination of high resolution patterning with end-functional chemistry enables the assembly of 1D nanostructures in an orderly fashion. The basic requirements for this approach are: molecular-scale lithographic patterning; control over nanostructure length; and facile end-functional chemistry. We believe this may be a viable avenue toward the integration of these materials in complex nanoarchitectures.

1. Schvartzman, M. and S.J. Wind, *Robust Pattern Transfer of Nanoimprinted Features for Sub-5-nm Fabrication.* Nano Letters, 2009. **9**(10): p. 3629-3634.
2. Zheng, M., et al., *Structure-based carbon nanotube sorting by sequence-dependent DNA assembly.* Science, 2003. **302**(5650): p. 1545-1548.
3. Zheng, M., et al., *DNA-assisted dispersion and separation of carbon nanotubes.* Nature Materials, 2003. **2**(5): p. 338-342.

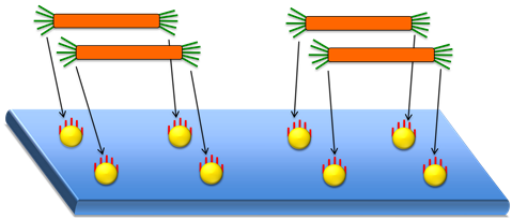

Figure 1. Schematic of 1D nanostructure attachment to functionalized nanodot anchors.

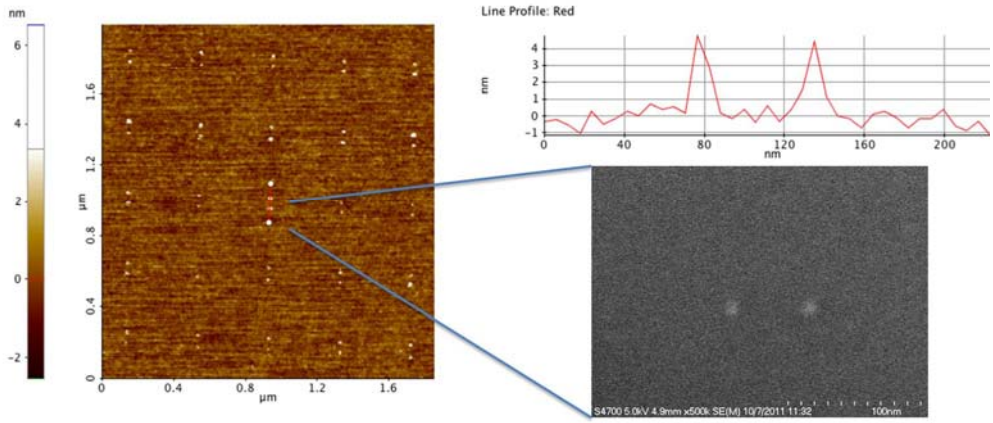

Figure 2. AFM and SEM (inset) images of the nanodot-anchors before functionalization. Comparison between AFM and SEM shows that they are spherical in shape, with a diameter of ~ 4-5 nm.

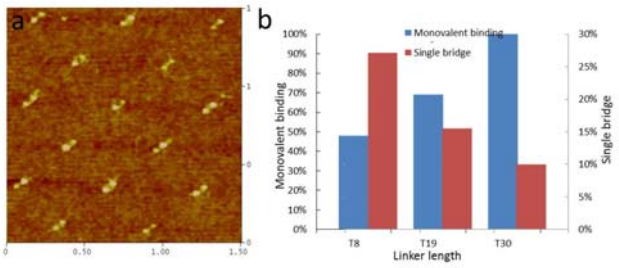

Figure 3. (a) AFM image of DFX-DNA attached to pairs of nanodot anchors. Bridging of the dots is achieved for each pair. Lateral monovalent attachment is also observed. (b) Yield of single DFX bridging and monomeric binding as a function of ssDNA linker length.

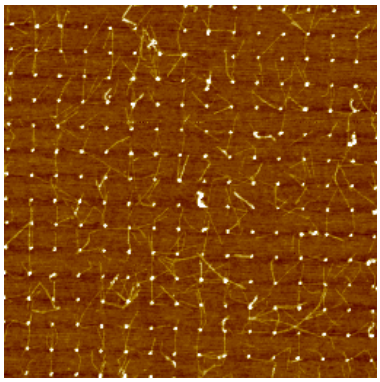

Figure 4. AFM image of SWNT segments attached to amine-functionalized nanodot anchors arranged in a square grid with 200 nm spacing.