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DNA origami templated self-assembly of discrete length single wall carbon nanotubes†

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Constructing intricate geometric arrangements of components is one of the central challenges of nanotechnology. Here we report a convenient, versatile method to organize discrete length single-walled carbon nanotubes (SWNT) into complex geometries using 2D DNA origami structures. First, a size exclusion HPLC purification protocol was used to isolate uniform length, SWNTs labelled with single stranded DNA (ssDNA). The nanotube-bound ssDNAs are composed of two domains: a SWNT binding domain and a linker binding domain. Although initially bound to the SWNTs, the linker domain is displaced from the surface by the addition of an external ssDNA linker strand. One portion of the linker strand is designed to form a double helix with the linker binding domain, compelling the DNA to project away from the SWNT surface. The remainder of the linker strand contains an ssDNA origami recognition sequence available for hybridization to a DNA origami nanostructure. Two different 2D DNA origami structures, a triangle and a rectangle, were used to organize the nanotubes. Several arrangements of nanotubes were constructed, with defined tube lengths and inter-tube angles. The uniform tube lengths and positional precision that this method affords may have applications in electronic device fabrication.

Introduction

Single-walled carbon nanotubes are among the most promising nanomaterials with projected uses in electronic, composite, sensor, and biomedical applications.[1,2] Compared to conventional semiconductor materials, they exhibit superior properties such as higher conductance, greater mobility, and chemical inertness, making them ideal components of field-effect transistor devices (FETs).[3,4] There have been many advances in the fabrication of 1D SWNT FET devices, and recently there were several reports of 2D SWNT assemblies.[5,6] Winfree and coworkers used LNA linkers to assemble SWNT cross junctions on rectangular DNA origami, where one device exhibited stable field effect transition behavior.[5] Törmä and coworkers used biotin–streptavidin interactions to create similar SWNT cross junctions on rectangular DNA origami.[6] However, neither method takes advantage of the convenience and versatility of unmodified DNA–DNA hybridization for nanotube organization. In addition, different lengths of SWNTs exhibit unique physical and electrical properties including absorbance, fluorescence and electric conductivity;[7–9] thus, for FET device applications it was imperative to develop protocols to separate heterogeneous populations of nanotubes.

With agitation, single stranded DNA will attach to SWNTs resulting in nanotube dispersion.[10,11] The strong Pi–Pi interaction between the bases within the DNA strand and the sidewall of the SWNT causes the DNA to wrap around the nanotube, forming the SWNT–DNA complex. It has been shown that certain DNA sequences can be used to separate different types of SWNTs,[12] and several methods have been used to separate the tubes based on length, including gel electrophoresis,[13] centrifugation[14] and size exclusion HPLC.[15] Zheng *et al.* reported a size exclusion HPLC protocol, with 200 nm, 100 nm, and 30 nm pore size columns arranged in series to separate DNA labeled SWNTs with lengths ranging from 500 nm to 1000 nm. Here we use a similar protocol to separate the DNA labeled nanotubes into different populations for subsequent organization by DNA origami structures.

DNA nanotechnology represents a massively parallel platform to assemble and organize heterogeneous nanoscale components.[16] Designing and constructing DNA nanostructure scaffolds is quite simple because of the reliability of DNA base pair interactions, the predictable structure of DNA double helices, and the self-assembling properties of single stranded DNA. The development of the DNA origami method has allowed the construction of arbitrary 2D and 3D nanoscale shapes that can be chemically modified at hundreds of

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addressable positions.[17–19] Towards electronic device applications, DNA origami structures have been used to pattern metal nanoparticles, semiconductor nanoparticles, and carbon nanotubes.[20,21] Here, 2D DNA origami triangles and rectangles were used to capture 150 nm, HPLC purified, DNA labeled SWNTs. The uniform length nanotubes were organized into several patterns, with control over the inter-tube angles.

HPLC separation of SWNTs

The single stranded DNA label is composed of two domains, a nanotube binding domain with a repeating GT sequence that exhibits strong binding with the SWNT sidewalls, and a capture domain with a sequence selected for recognition by an external, ssDNA linker strand. The ssDNA label was mixed with an aqueous solution of SWNTs and sonicated for 2 h at 9 W. The solution mixture was subsequently centrifuged to remove aggregated bundles, and the supernatant was injected into an HPLC system that was configured with three size exclusion columns connected in series (0.2 mL min^{-1}, 1 × TBS buffer, UV-Vis detection at 260 nm). A typical HPLC profile is shown in Fig. S1;† several fractions were collected and examined with a transmission electron microscope. The TEM results (Fig. 1) revealed that the SWNTs were clearly separated by length, with each fraction containing a single SWNT population of uniform length (ranging from 100 nm to 500 nm).

DNA origami organization of uniform length SWNTs

In principle, SWNTs could be labeled with ssDNA that contains a domain for direct hybridization to a DNA origami structure. However, this would require that single stranded overhangs (probes) from the DNA origami structure could efficiently displace the corresponding DNA from the surface of the nanotube sidewall. Although desorption of ssDNA from SWNTs has been reported, the process is prohibitively slow.[5] A more plausible alternative, and the one employed here, is to use an intermediate single stranded DNA linker molecule. One domain of the linker has a sequence complementary to part of the ssDNA label (bound to the nanotube surface), and the other contains a sequence that will hybridize to a DNA origami probe. The addition of excess single stranded linker to a solution of ssDNA labeled SWNTs displaces part of the ssDNA label from the nanotube surface, forming a DNA double helix with the linker strand. Compared to the first scenario, this process is expected to be more kinetically favorable. After purification, the unbound single stranded region of the linker strand is captured by DNA origami probes and secured in a fixed position.

We selected 150 nm long SWNTs (shown in Fig. 1E) for subsequent experiments. The HPLC isolated SWNTs were incubated with a ten-fold excess of linker strand for 48 hours so that the linker binding domain of the ssDNA label would be displaced from the surface of the nanotube. A Microcon centrifugal filter was used to remove excess linker strand from the solution.

Meanwhile, the triangular and rectangular DNA origami structures, with several linker probes displayed from their surfaces, were prepared. Initially, several different probe sequences were evaluated including a poly T and several random sequences, and the results show that the poly T probe resulted in a much higher capture yield (shown in Fig. S2 and S3†). Rectangular origami structures with two perpendicular rows of poly T linker probes were prepared and incubated with the purified, DNA labeled, 150 nm length SWNTs for 30 minutes at room temperature. The atomic force microscope (AFM) images shown in Fig. 2B and S4† confirm 50% yield of origami bound nanotubes. Longer incubation times induced aggregation, possibly because the length of the SWNTs is

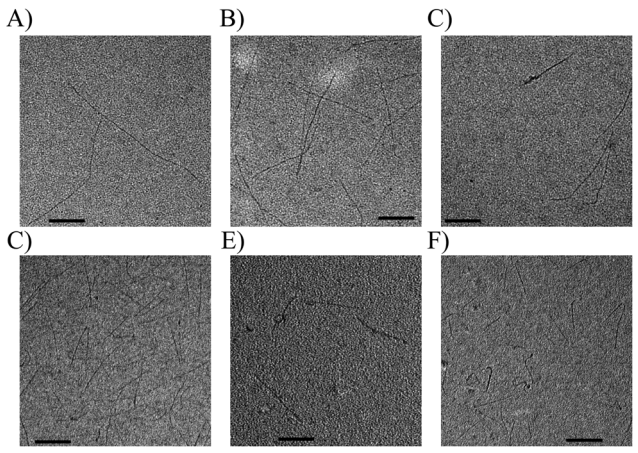

Fig. 1 DNA labeled SWNTs separated by HPLC. (A), (B), (C), (D), (E), (F) are TEM images of HPLC separated fractions with length 450, 300, 200, 170, 150 and 100 nm (scale bar: 100 nm).

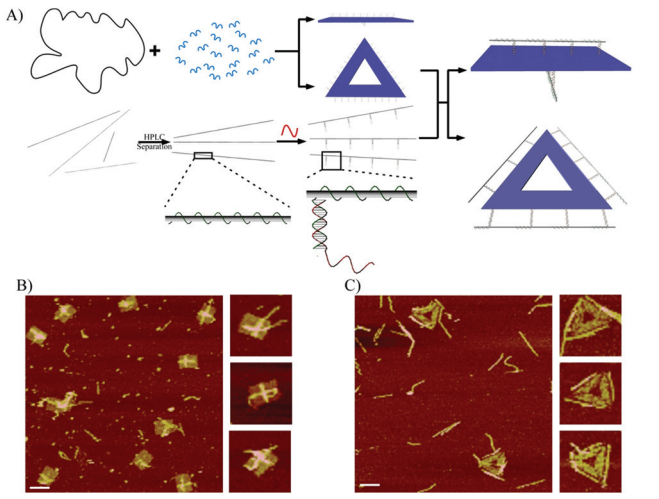

Fig. 2 (A) DNA origami–SWNT co-assembly schematic. (B), (C) AFM images of SWNTs organized by rectangular origami and triangular origami, respectively (scale bar: 100 nm).

longer than the DNA origami structures and may increase the potential to crosslink different origami. To further evaluate this, 200 nm, 350 nm and 450 nm SWNTs were also considered. The results show (Fig. S5–S7†) that the longer tubes tend to form aggregated structures. With the extra linker strands displayed from the surface of the tubes, the chance to cross link origami is increased. Finally, triangular origami structures with one row of poly T probes along each arm (3 rows total) were prepared and incubated with the purified DNA labeled SWNTs for 15 minutes at room temperature. The AFM images shown in Fig. 2C and S8† reveal approximately 40% yield of origami bound nanotubes. Despite the reasonable yield, it is obvious from the AFM images that many free SWNTs remained and further purification is needed.

Conclusion

In summary, we demonstrated that DNA origami nanostructures can be used to arrange SWNT of fixed length into complex, 2D patterns. In addition to dispersing SWNTs in aqueous solution, we developed a strategy in which ssDNA molecules can serve as efficient labels of SWNTs, for subsequent recognition by DNA origami probes. Our method of recognition is based on DNA–DNA hybridization, a very convenient interaction to employ. Several arrangements of nanotubes were constructed, with defined tube lengths and inter-tube angles. The uniform tube lengths and positional precision that this method affords may have applications in electronic device fabrication.

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