Carbon Nanotubes

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Grafting Single-Walled Carbon Nanotubes with Highly Hybridizable DNA Sequences: Potential Building Blocks for DNA-Programmed Material Assembly**

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This communication reports a method to realize controllable self-assembly of single-walled carbon nanotubes (SWNTs). Material self-assembly has been a rapidly evolving research area targeted at integrating nanoscale building blocks into functioning devices. To this end, various researchers have shown that DNA molecules can serve especially well to create highly definable supramolecular networks that can be used to advantage for the programmed self-assembly of objects with nanometer precision.[1–6]

It has been demonstrated that DNA hybridization can induce the self-assembly of gold nanoparticles.[3,4] So far, DNA has been used to guide the assembly of gold nanoparticles into discrete structures with defined numbers of particles,[3] as well as one-dimensional (1D)[5] or two-dimensional (2D)[6] arrays. Carbon nanotubes (CNTs) have attracted significant research interest since they were found in 1991 by Iijima.[7] To enrich the family of objects that can be used for DNA-directed self-assembly, researchers have tried to covalently conjugate DNA to CNTs and have attempted to use DNA hybridization to drive the self-assembly of CNTs.[8] However, besides various potential technical problems when dealing with chemical coupling reactions, most of the attempts did not succeed in getting a high-density conjugation of DNA onto the CNTs, and the hybridizability of the DNA–CNT conjugates was usually not considered or evaluated. The lowered hybridizability of DNA when conjugated to other materials could cause problems or unexpected difficulties in achieving programmed material assembly.

Recently, Zheng et al.[9] reported a method to disperse SWNTs in water by DNA wrapping. This strategy enabled the length separation of SWNTs by chromatography or gel electrophoresis,[9b,10] and it has excited researchers to refine this technique and to find applications for the DNA-wrapped SWNTs.[11,12] In this work, we employ DNA-wrapped SWNTs to construct a self-assembly system. By grafting highly hybridizable DNA sequences onto the DNA-wrapped SWNTs, we are able to demonstrate the reversible self-assembly of SWNTs, switched by DNA hybridization.

To realize DNA-hybridization-driven self-assembly of SWNTs, the following steps are employed (shown in Figure 1a): 1) SWNTs are wrapped with strand **1** to form the SWNT–**1** conjugate; 2) strands **3** and **4** are added to two separate SWNT–**1** solutions to get the SWNT–[**1**,**3**] and SWNT–[**1**,**4**] conjugates, respectively; 3) SWNT–[**1**,**3**] and

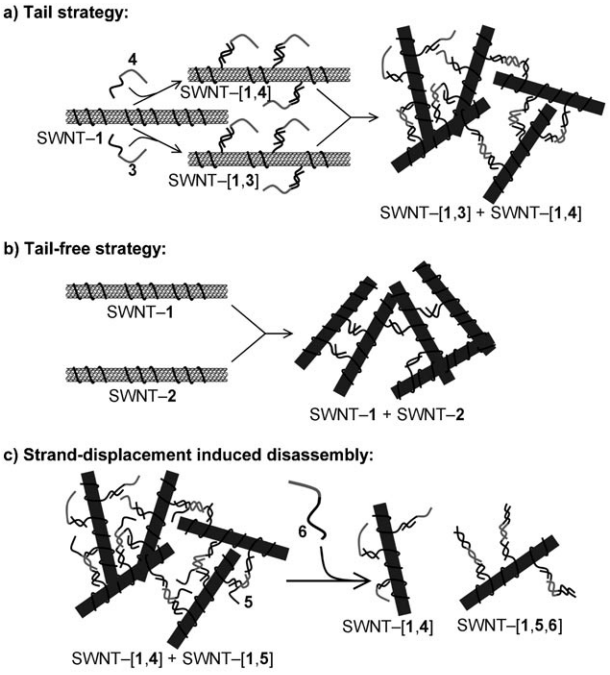

Figure 1. Self-assembly of DNA-grafted carbon nanotubes into 3D aggregates upon hybridization, and disassembly of the as-formed aggregates by DNA-strand displacement. a) Tail strategy: hybridization happens between SWNT–[**1**,**3**] and SWNT–[**1**,**4**] with grafted DNA tails. b) Tail-free strategy: hybridization happens between SWNT–**1** and SWNT–**2**, with the two complementary sequences embedded in the disperser strands **1** and **2**. c) Reversal of SWNT aggregation by using a DNA-strand-displacement strategy: In this case, strand **3** is replaced by **5**, and the base pairing between **5** and **4** that is responsible for holding the SWNT aggregates can then be disrupted by adding strand **6** as a stripper strand. See Figure S1 in the Supporting Information for the same figure with color-coded DNA strands.

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SWNT–[**1**,**4**] are mixed together in an appropriate buffer to make assembly happen. The sequences of strands **1**, **3**, and **4** are chosen so that hybridizations can happen between strands **3** or **4** and strand **1** to produce hybridizable tails on the SWNTs. These hybridizations (see Figure 1 a) only use half of the sequences in strands **3** and **4**, thereby leaving 16 unpaired bases (colored in blue and green in Figure S1 in the Supporting Information) in **3** and **4** as hybridization "tails" on the resulting DNA–SWNT conjugates, SWNT–[**1**,**3**] and SWNT–[**1**,**4**]. This hybridization strategy is referred to as the tail strategy in the following text.

Alternatively, it is also possible to covalently fuse the two hybridizing sequences with $d(GT)_{20}$ (the dispersing sequence) during DNA synthesis, and the resulting strands are strands **1** and **2**. Hybridization between SWNT–**1** and SWNT–**2** (termed as a tail-free strategy in contrast to the tail strategy mentioned above) can also result in SWNT aggregates (Figure 1 b). However, we expect the tail strategy (Figure 1 a) will avoid serious wrapping of the hybridization sequences onto the SWNTs, which happens during the sonication process in order to disperse the carbon nanotubes. Therefore, the tail strategy in Figure 1 a should greatly improve the hybridization kinetics compared to that of the tail-free strategy during the formation of SWNT aggregates. We evidenced this by using agarose gel electrophoresis to analyze the hybridization kinetics.

As shown in Figure 2, grafting of hybridization sequences as tails onto the DNA-wrapped carbon nanotubes greatly enhanced the speed of hybridization of the carbon nanotubes.

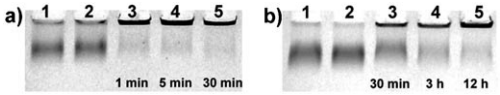

Figure 2. 0.5 % agarose gel electrophoresis of the assembled SWNT aggregates between a) SWNT–[**1**,**3**] and SWNT–[**1**,**4**] and b) SWNT–**1** and SWNT–**2**. Lanes 1–2 in both gels are the SWNT–DNA conjugates before hybridization, that is, SWNT–[**1**,**3**] and SWNT–[**1**,**4**] in (a) and SWNT–**1** and SWNT–**2** in (b). Lanes 3–5 in the two gels are the assembly products after mixing of corresponding SWNT–DNA conjugates as in lanes 1 and 2. The different hybridization times for lanes 3–5 in (a) and (b) are indicated in the corresponding lanes. These results clearly indicate that the tail strategy (a) has much faster hybridization kinetics than the tail-free strategy (b).

In the case of the tail-free strategy with directly embedded hybridizing sequences within strands **1** and **2** (Figure 1 b), the resulting SWNT–**1** and SWNT–**2** conjugates begin to aggregate in about 30 minutes (about 30–50 % of the SWNTs form aggregates, as estimated from the gel in Figure 2), and even after more than 12 h, there are still some unhybridized carbon nanotubes forming a discernible moving band in the gel. The concentrations of carbon nanotubes for the comparative hybridization experiments shown in Figure 2 were adjusted to be as close as possible, based on their optical absorbances at 652 nm. The gels shown in Figure 2 had been run for about 12 min before the pictures were taken. Hybridization of DNA–SWNT conjugates during electrophoresis should be quite minor because of the dramatically inhibited diffusion of carbon nanotubes in the gel matrix and the relatively short running time. Usually, non-aggregated SWNTs, after being loaded into the gel wells, run completely into the gel in about 2–3 minutes, so hybridizations of SWNTs residing in the gel wells (as free solution species) should also be minor considering most of the hybridization times (>5 min) we used. All of these factors should minimize possible hybridizations during the gel electrophoresis and thus make gel electrophoresis well suited for characterization of the self-assembly of SWNTs.

The SWNT aggregates formed by DNA hybridization were further checked by atomic force microscopy (AFM; Nanofirst-3000, Haizisi Co., Ltd., China). Samples were deposited on an Mg^{2+}-treated mica surface and analyzed by tapping-mode AFM. Figure 3 shows the dramatic morphology change for the carbon nanotubes after the aggregates form. In the SWNT–[**1**,**3**] or SWNT–[**1**,**4**] samples before they are mixed together, the carbon nanotubes are well dispersed and uniformly distributed on the mica substrate. After the samples have been combined, the carbon nanotubes gradually form large aggregates of up to 10 μm in size, as evidenced by our AFM imaging. The AFM results are consistent with the gel electrophoresis in Figure 2 and provide a direct view of the hybridization-driven SWNT aggregates.

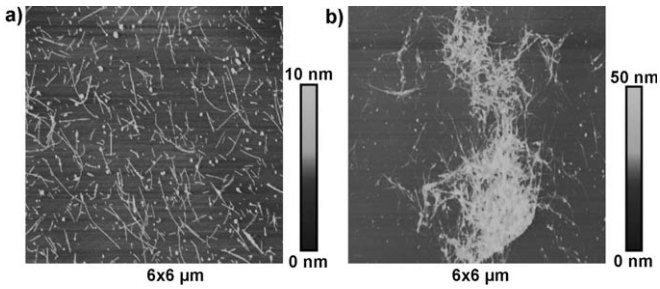

Figure 3. AFM images of the DNA-conjugated SWNT–[**1**,**3**] a) before and b) after hybridization with SWNT–[**1**,**4**]. See Figures S3 and S4 in the Supporting Information for more AFM images showing the aggregated and dispersed SWNT samples.

SWNT–[**1**,**3**] and SWNT–[**1**,**4**] almost immediately formed aggregates that couldn't penetrate into a 0.5 % agarose gel after the two conjugates were mixed together in a 0.5 × Tris/borate/EDTA, (TBE, Tris = tris(hydroxymethyl)aminomethane, EDTA = ethylenediaminetetraacetate disodium salt) buffer containing 30 mM NaCl and an extra 10 mM EDTA (see the Experimental Section in the Supporting Information. The agarose gel in Figure 2 a indicates that even after a very short (1 min) hybridization time, there are almost no carbon nanotubes that can move into the gel. Most of them (>90 %) form aggregates and are retained in the gel-loading well. Actually, the difference between the 1-min and 30-min hybridizations for the tail strategy is hard to distinguish, which implies very fast hybridization kinetics.

As the aggregates formed above are held together by DNA base-pairing, we should be able to disrupt them by using a DNA-strand-displacement strategy.[13] To realize this, DNA strand **3** was replaced by strand **5** (Figure 1 c), which had an

extension of 16 extra bases (colored in orange in Figure S1 in the Supporting Information). The as-constructed SWNT–[**1**,**5**] conjugate can similarly hybridize with SWNT–[**1**,**4**] to form aggregates. To these aggregates was added DNA strand **6**, which competes with strand **4** in the duplex formed between **4** and **5** (termed the **4**–**5** duplex). As strand **5** can fully base pair with strand **6** to form a 32-bp **5**–**6** duplex, which has double the length of the **4**–**5** duplex, strand **4** is gradually stripped away from strand **5** because of this hybridization competition (Figure 1c). Finally, the SWNT aggregates are disassembled and redispersed in the solution. Gel electrophoresis was used to demonstrate this process (see Figure 4). This aggregation–

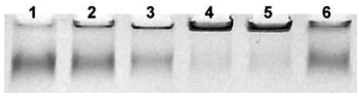

Figure 4. 0.5% agarose gel electrophoresis results that demonstrate the DNA-hybridization-switched reversible assembly and disassembly of SWNTs. Lanes 1–3 correspond to unhybridized SWNT–[**1**,**3**], SWNT–[**1**,**4**] and SWNT–[**1**,**5**], respectively; lane 4 corresponds to the aggregates formed between SWNT–[**1**,**4**] and SWNT–[**1**,**3**]; lane 5 corresponds to the aggregates formed between SWNT–[**1**,**4**] and SWNT–[**1**,**5**]. After introduction of stripper strand **6** (see Figure 1c), the aggregates in lane 5 are disrupted into individually dispersed SWNTs, as shown in lane 6.

dispersion process was further verified by AFM imaging and the corresponding data are given in Figure S5 in the Supporting Information.

The carbon nanotubes, after aggregation happens, should tend to precipitate from the solution. In addition to the gel electrophoresis experiment, we have also used a centrifugation-assisted precipitation technique to visually observe the precipitate formed as a result of the aggregation of the DNA–SWNT conjugates as well as the redispersion of the as-formed precipitate after adding stripper strand **6** (see Figure S2 in the Supporting Information). This result further reveals the sharp contrast between the dispersed and aggregated states of the DNA–SWNT conjugates.

Based on the strategy we described in an earlier publication,[12] we could also use this new building block for the assembly of linear gold-nanoparticle (AuNP) arrays (Figure 5). To achieve this goal, 6-nm AuNPs were first

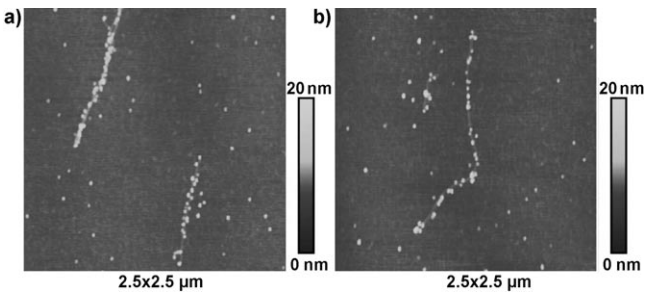

Figure 5. AFM images of the AuNP–SWNT linear assemblies obtained by hybridizing the tail-bearing SWNTs with 6-nm gold nanoparticles premodified with complementary DNA sequences. a) and b) are images from the same sample.

modified with DNA sequences complementary to the tails grafted on the SWNTs (see Figure S6 in the Supporting Information for the assembly strategy). Thereby, linear AuNP arrays could be formed by combining DNA–AuNPs with DNA–SWNTs (Figure 5 and Figure S8 in the Supporting Information). Agarose gel electrophoresis (see Figure S7 in the Supporting Information) was then used to isolate the assembly products by using the method we developed before.[12]

Besides the aggregation strategy as shown in Figure 1, we have also found that the use of a DNA linker to bridge the tails grafted on different carbon nanotubes can similarly result in SWNT aggregates (Figures S9 and S10 in the Supporting Information). This finding may be further elaborated in the future to build sensing assays for DNA detections by taking advantage of the unique physical properties of carbon nanotubes and the well-developed sensing strategies based on gold nanoparticles.

In conclusion, we have developed a method to graft highly hybridizable DNA sequences onto DNA-wrapped single-walled carbon nanotubes. Our experiments show that these DNA-grafted carbon nanotubes have very fast hybridization kinetics compared to those with the hybridizing sequences directly embedded within the disperser strands. This is because the hybridization sequences in the latter case have a strong tendency to wrap around the carbon nanotubes during sonication and therefore dramatically decrease their base-paring ability. As a step forward, we have also fulfilled a hybridization-switched aggregation and dispersion of carbon nanotubes by using a DNA-strand-displacement strategy. Due to the appealing physical and chemical properties of carbon nanotubes, the tailed DNA–SWNT conjugates we have constructed in this work might be used as potential building blocks for DNA-programmed material assembly; these building blocks are expected to parallel or even outperform the regularly employed objects, such as gold nanoparticles. Therefore, important applications such as the building of various electronic or sensing devices may be expected in the future.

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