Communication

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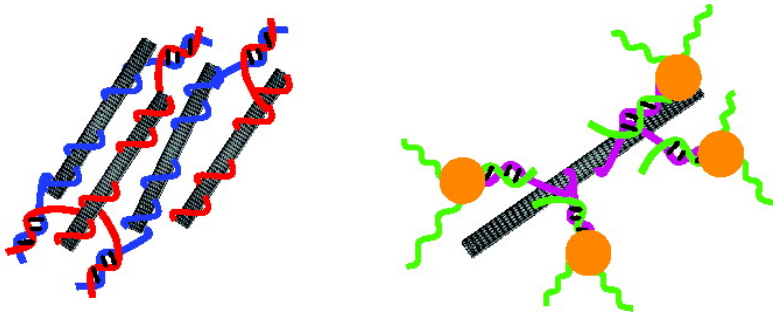

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DNA-Directed Assembly of Single-Wall Carbon Nanotubes

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This paper explores the use of DNA hybridization to manipulate single-wall carbon nanotubes (SWNTs), including reversible aggregation of SWNT and formation of SWNT−gold nanoparticle (AuNP) hybrid structures. This work is along the effort of using biomacromolecules for controlled assembly of SWNTs. We have examined this strategy by gel electrophoresis, dynamic light scattering (DLS), optical absorption spectra, and atomic force microscopy (AFM) imaging.

SWNTs are leading building blocks for nanomaterials and have great potential in electronics, optics, mechanics, thermal transportation, and biosensing.[1−3] A key challenge for the application of SWNTs is how to assemble them into desired large architectures, which attracts extensive scientific researches. One approach is to conjugate SWNTs with information-containing molecules that can guide SWNTs for self-assembly. Among all candidate molecules, DNA is a promising choice for its excellent molecular recognition capability. A rich body of studies has demonstrated that DNA can be programmed to self-assemble into sophisticated nanostructures, and many strategies are available to engineer DNA nanostructures.[4−6] DNA has also been reported to be able to wrap onto SWNTs for SWNTs' dispersion and DNA transportation.[7−9] Thus, it is conceivable to apply DNA for controllable assembly of SWNTs. Herein, we report our initial work in this direction: using DNA hybridization to control SWNT aggregation and SWNT−AuNP heteroaggregation. Conceptually, this strategy originates from the works of using DNA to control the aggregation of AuNPs.[10,11]

The overall strategy contains two steps (Figure 1): (1) A pair of complementary DNA single strands separately complex to component nano-objects, SWNTs or AuNPs. (2) Upon mixing the two complexes, the complementary DNA strands recognize and associate with each other and bring the nano-objects together to form aggregates of SWNTs or SWNT−AuNP hybrids. For SWNTs, DNA single strands physically complex with them; for AuNPs, thiolated DNA strands are used, which readily adsorb onto AuNPs through the formation of S−Au bonds.[10,11]

We prepared DNA-complexed SWNTs by adapting a reported method.[12] Briefly, SWNTs were dispersed into aqueous solution by sonication in SDS solution. Then the SWNT suspension was incubated with DNA single strands. Undispersed SWNTs, SDS, and free DNA single strands were removed by ultracentrifugation, dialysis against water, and filtration, respectively. The resulting DNA−SWNT complexes were well-dispersed in water.

We have investigated the DNA-mediated SWNT aggregation with agarose gel electrophoresis. Upon mixing, DNA−SWNT complexes aggregate through DNA hybridization. The SWNT aggregates have larger volumes than individual DNA−SWNT complexes. Thus, the SWNT aggregates are expected to migrate slower than individual SWNTs or to be unable to penetrate into the gel at all. This phenomenon is observed in the electrophoresis experiment (Supporting Information, Figure S1). Individual SWNTs appear as sharp, fast-moving bands, whereas the mixtures move much slower and appear as continuous smears, which correspond

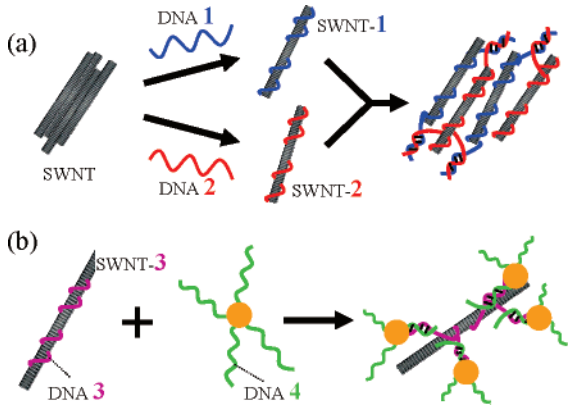

Figure 1. DNA hybridization controls (a) aggregation of single-wall carbon-nanotubes (SWNTs) and (b) formation of SWNT−gold nanoparticle (AuNP) hybrid structures. Note that we do not exactly know how DNA interacts with SWNTs.

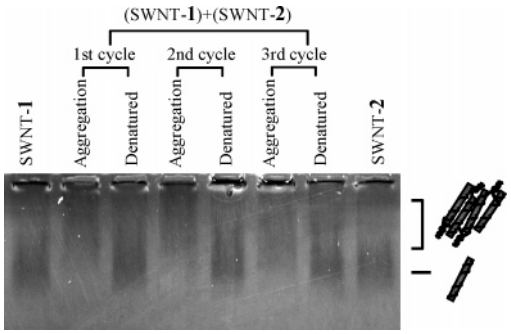

Figure 2. Electrophoretic analysis of reversible SWNT aggregation−dissociation by thermal cycling: aggregation, slowly annealed; dispersion, thermal denatured. Materials in each lane are indicated above the gel image and the chemical identity of each band in the gel is indicated at the right.

to different extents of aggregation. Briefly exposing the sample to a high-temperature (95 °C), DNA duplexes dissociate and the aggregates dissociate too. Then the sample is quenched to 4 °C and immediately loaded for electrophoresis; the DNA will not be able to recognize each other to form duplexes, thus, the SWNTs remain as individual SWNTs. In the gel, they return to a sharp, fast-moving band.

DNA duplexes form at low temperatures and dissociate at high temperatures. It is a reversible process and can be repeated over and over again. Correspondingly, the SWNT aggregation−dispersion is reversible and can be repeated as well (Figure 2). In the gel, SWNTs oscillate between sharp, fast-moving, individual SWNT bands and slow-moving SWNT aggregate smears.

DLS measurement further supports the formation of SWNT aggregates. DLS directly measures the size distribution of particles in the solutions. When modeled as spheres, the two individual DNA-SWNT complexes have apparent radiuses of 58 and 54 nm, respectively. Upon mixing, the apparent radius increases to 81 nm.

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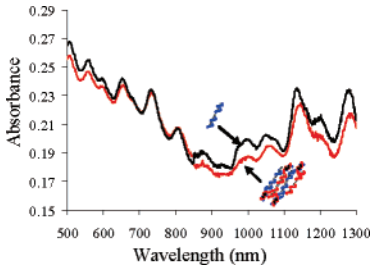

Figure 3. Spectroscopic characterization of SWNT aggregation. The arrows indicate the changes.

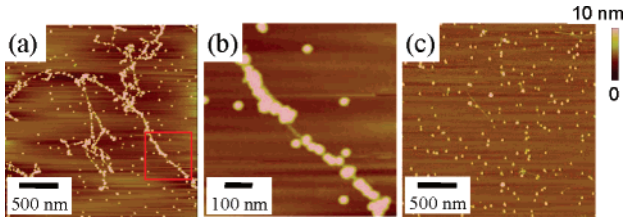

Figure 4. Atomic force microscopy (AFM) images of hybrid SWNT−AuNP structures formed by DNA hybridization: (a) SWNT−AuNP hybrid structures (complementary DNA strands used), (b) a close-up view of the boxed area in panel a, and (c) individual SWNTs and AuNPs (noncomplementary DNA strands used).

Note that the absolute radius values are not accurate because we used a sphere model, which is different from the geometry of the SWNT. However, the apparent values indicate the relative physical sizes of the particles (individual SWNTs or SWNT aggregates). The substantial increase of the apparent radius is consistent with the SWNT aggregation.

SWNT aggregation affects the optical properties of the SWNTs (Figure 3). Upon aggregation, the absorption spectra of the SWNTs exhibit clear changes in the NIR range (800−1300 nm), which corresponds to the interband transitions from semiconducting SWNTs.[12,13] Most notable changes are the shapes and the maximum absorption wavelengths (λ_{max}) of the absorption peaks. The absorption peaks have red shifts up to 16 nm. In the visible light range, aggregation decreases SWNT adsorptions, but has no effect on λ_{max}.

We further applied this strategy to prepare SWNT−AuNP hybrid structures (Figure 1b and Figure 4). DNA-conjuated AuNPs were prepared according to literature.[10] Briefly, thiolated DNA single strands were incubated with AuNPs and the solution ionic strength was gradually increased. This process formed S−Au bonds and many DNA strands were linked to each AuNP. Upon mixing DNA-complexed SWNTs and excess DNA−AuNPs, complementary DNA base-paired with each other, which brought AuNPs to bind to SWNTs. An AFM image clearly showed the formation of SWNT−AuNP hybrid structures (Figure 4). When noncomplementary DNA strands were used, no such heterostructures were observed and both SWNTs and AuNPs were randomly distributed. This control experiment confirms that the DNA hybridization is the driving factor for the formation of the SWNT−AuNP hybrid structures. The overall SWNT−AuNP structure is similar to a previously reported structure in which metallic nanoparticles are synthesized along SWNTs.[14]

The proposed strategy works well as the experimental data show. However, many important questions remain. What are the structures of the DNA−SWNT complexes? DNA strands might completely wrap on SWNTs and strongly interact with the side walls of SWNTs. It is also possible that only some DNA segments interact with SWNTs but other segments do not directly interact with SWNTs and protrude out into solutions. Another question is how did the DNA hybridization happen? The DNA wrapped on SWNTs might interact with each other. More likely, the DNA association involves some loose DNA segments that do not strongly interact with SWNTs. What DNA structures form upon hybridization? Those questions must be addressed before using this strategy to assemble sophisticated SWNT-based nanostructures.

In summary, we have demonstrated using DNA hybridization to form SWNT aggregates and SWNT−AuNP heteroaggregates. Such aggregations cause some changes in optical properties of the SWNT as suggested by the absorbance. We expect that the photoluminescence of SWNTs will have significant changes as well. More importantly, it is possible to use self-assembled, sophisticated DNA nanostructures to organize SWNTs into complex architectures. The hybrid structures might provide an excellent platform for integrated nanodevices: zero-dimensional nanoparticles (NPs, not necessary to be AuNPs) can sense or react to environments individually and locally and communicate with each other through the long, one-dimensional SWNTs.

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Supporting Information Available: Experimental method and additional experimental data. This material is available free of charge via the Internet at http://pubs.acs.org.

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