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DNA-Directed Self-Assembling of Carbon Nanotubes

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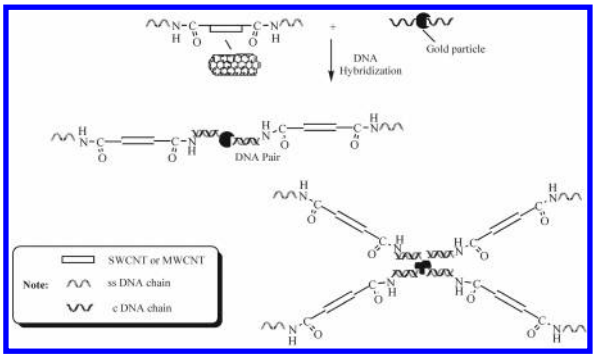
Since Iijima's discovery in 1991,[1] carbon nanotubes, including single-wall carbon nanotubes (SWNTs) and multiwall carbon nanotubes (MWNTs),[2] have been shown to possess superior electronic, thermal, and mechanical properties to be attractive for a wide range of potential applications.[2,3] The use of carbon nanotubes as "building blocks" in nano-/microelectronic devices could revolutionize the electronic industry in the same way that the microchips have revolutionized the computer industry. However, it has been a long-standing big challenge to efficiently integrate the carbon nanotube "building blocks" into multicomponent/multifunctional structures or devices. Generally speaking, multifunctional structures can be prepared by (i) self-assembly of small-sized entities into larger structures ("bottom-up" approach) and/or (ii) systematic reduction of large systems down to smaller sizes to produce multifunctional nanoscale structures ("top-down" approach).[3] Although various synthetic and post-synthesis fabrication methods have been devised for the preparation of carbon nanotubes with certain specific structural features (e.g., aligned, micropatterned),[4] the formation of multicomponent (and, hence, multifunctional) nanotube self-assemblies from preformed individual carbon nanotubes has been much less discussed in the literature.[5] On the other hand, DNA chains have been used to create various functional structures and/or devices through the sequence-specific pairing interactions.[6] Recently, the DNA-based biomolecular recognition principle has also been applied to carbon nanotubes to construct not only nanotube electronic devices (e.g., field-effect transistors),[7] by DNA-directed placements of carbon nanotubes attached with single-strand DNA chains (ssDNAs) on a substrate region-specifically grafted with complimentary DNA chains (cDNAs), but also carbon nanotube−DNA electrochemical sensors,[8] by chemically attaching a carbon nanotube electrode with ssDNA chains for hybridization with redox-labeled cDNA chains. As far as we are aware, however, the potential use of DNA-pairing interactions for creating multicomponent structures from multiple carbon nanotubes, including SWNTs and MWNTs, in solution has been largely neglected. In addition to the use of certain ssDNA-attached carbon nanotube electrodes for DNA sequence sensing via hybridization with redox-labeled cDNA chains,[8b] Moghaddam and co-workers[8c] have previously demonstrated that cDNA-grafted gold nanoparticles could be used for visualizing the ssDNA functional sites on the nanotubes by the sequence (site)-specific hybridization and electron microscopic imaging of the nanoparticles. The above work prompted us to exploit the use of DNA hybridization for DNA-directed self-assembling of multiple carbon nanotubes into various multicomponent structures. In this communication, we present results from our recent work on the DNA-directed self-assembling of multiple carbon nanotubes and gold nanoparticles into multicomponent structures.

Scheme 1. Schematic Representation of Procedures for DNA-Directed Self-Assembling of Multiple Carbon Nanotubes and Nanoparticles



Scheme 1 shows the reaction steps for the DNA-directed self-assembling of multiple carbon nanotubes using the gold nanoparticles as a linkage, which involves the acid (HNO_3) oxidation of carbon nanotubes to introduce carboxylic end groups[9] for ssDNA grafting. The ssDNA-attached carbon nanotubes were then subjected to hybridization with cDNA chains grafted on gold nanoparticles through the highly specific thiol−gold interaction.[10]

In a typical experiment, we carried out the acid oxidation of both MWNTs generated from pyrolysis of iron (II) phthalocyanine[11] and SWNTs (Carbon Nanotechnologies Inc.) in an aqueous solution of concentrated nitric acid (70 wt%) under ultrasonification at room temperature for 8 h. After purification by centrifugation, dialysis, and filtration,[9] the resultant acid-oxidized carbon nanotubes were redissolved in water for chemical bonding with amino-end-functionalized ssDNA chains (i.e., [AmC6]TTGACACCAGACCAACTGGT-3′) through the amide formation in the presence of 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC) coupling reagent for overnight at room temperature.[8b] The products from the above reactions are designated as ssDNA−MWNTs and ssDNA−SWNTs, respectively. Meanwhile, gold nanoparticles were prepared from an aqueous solution of $HAuCl_4 \cdot 3H_2O$ and sodium citrate according to the published procedure,[12] followed by end-attachment with cDNA chains of the sequence [HSC6]ACCAGTTGGTCTGGTGTCAA-3′ via the strong thiol−gold interaction[10] (designated as: cDNA−Au). The DNA hybridization was then performed by keeping the cDNA−Au nanoparticles with ssDNA−MWNTs and/or ssDNA−SWNTs in an aqueous solution in a water bath at 42 °C for 2 h. The unpaired DNA and Au, if any, could be removed by dialysis through membranes of an appropriate pore size. A droplet of the resultant solution (0.03 mg/mL) was then deposited on a freshly cleaved mica surface and dried up in air at the ambient atmosphere for their subsequent characterization on an atomic force microscope (AFM, Digital NanoScope III).

Figure 1 shows typical AFM images for the acid-oxidized

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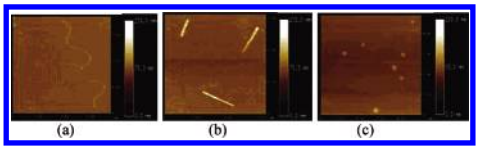

Figure 1. Typical AFM image of (a) the acid-oxidized SWNTs (scanning area: 3.75 μm × 3.75 μm; vertical scale bar: 150 nm), (b) the acid-oxidized MWNTs (scanning area: 7.80 μm × 7.80 μm; vertical scale bar: 150 nm), and (c) the as-prepared gold nanoparticles (scanning area: 5.00 μm × 5.00 μm; vertical scale bar: 100 nm).

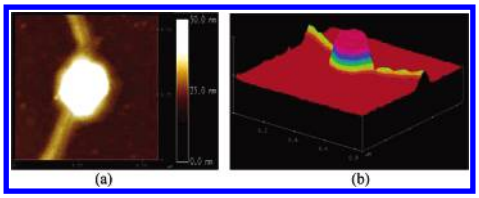

Figure 2. Typical AFM image of (a) the self-assembly of ssDNA−MWNTs and cDNA−Au nanoparticle (scanning area: 0.55 μm × 0.55 μm; vertical scale bar: 50 nm) and (b) the 3-D surface plot of (a) with different color codes (scanning area: 0.85 μm × 0.85 μm).

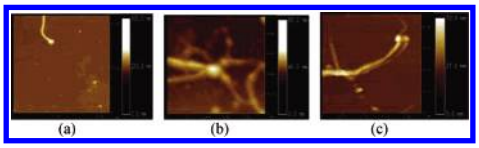

Figure 3. Typical AFM image of (a) the self-assembly of a ssDNA−SWNT and ssDNA−MWNT through a cDNA−Au nanoparticle (scanning area: 5.60 μm × 5.60 μm; vertical scale bar: 300 nm), (b) multiple ssDNA−SWNTs and ssDNA−MWNTs connected with a cDNA−Au nanoparticle core (scanning area: 1.10 μm × 1.10 μm; vertical scale bar: 80 nm), and (c) three ssDNA-attached nanotubes connected by two cDNA−Au nanoparticles (scanning area: 1.15 μm × 1.15 μm; vertical scale bar: 50 nm).

SWNTs (Figure 1a) and MWNTs (Figure 1b), in which isolated nanotubes with a relatively short tubular length (<3 μm) are clearly evident. Figure 1c shows isolated gold nanoparticles with an average diameter of about 150 nm. The AFM images for ssDNA−SWNTs, ssDNA−MWNTs, and cDNA−Au nanoparticles show features similar to those of the corresponding images given in Figure 1, indicating no self-aggregation was caused by the attachment of DNA chains.

The DNA-directed self-assembling of carbon nanotubes was initially investigated by mixing ssDNA−MWNTs (0.03 mg/mL) with cDNA−Au nanoparticles (0.03 mg/mL) in an aqueous solution at 42 °C. As can be seen in Figure 2a, individual MWNTs were interconnected by the gold nanoparticle through the DNA hybridization. The three-dimensional surface plot of Figure 2a with different color modes revealed a "gap" between the nanoparticle and connected carbon nanotube with a separation distance of about 70 Å, corresponding to the full length of the DNA double-helix (dsDNA) linkage of 20 base pairs (Figure 2b).[13] No similar interconnected structure was observed in control experiments, in which the oxidized MWNTs/cDNA−Au, ssDNA−MWNTs/Au, or ssDNA−MWNTs/ssDNA−Au were mixed together under the same conditions, although nanotube junction(s) without the Au linkage could occasionally form through the intertube interaction in the deposits (ca. 5 out of 100) from some of the solutions.

To further confirm the DNA-directed self-assembling of carbon nanotubes and to prepare multicomponent nanotube self-assemblies, we carried out the DNA hybridization for a mixture solution of ssDNA−MWNTs, ssDNA−SWNTs, and cDNA−Au nanoparticles. Figure 3 clearly shows the formation of various self-assembled multiple carbon nanotube structures, including one SWNT connected with one MWNT through a nanoparticle (Figure 3a), multinanotubes connected to a single nanoparticle core (Figure 3b), and multinanotubes connected by multinanoparticles (Figure 3c), depending on the reaction conditions. Note, however, some branched structures with thin nanotubes end-attached onto the sidewall of thick nanotube arms are also seen in Figure 3b. The observed nanotube branches could be attributed to the possible formation of dsDNA double helix linkages between the tip-modified ssDNA−SWNTs and the sidewall-modified ssDNA−MWNTs through a common cDNA−Au nanoparticle, as the acid-oxidation reaction is known to introduce carboxyl groups at any defect sites even on the sidewalls of MWNTs while mainly at the tips of SWNTs.[3,9] Therefore, the above results, together with the fact that cDNA chains can be chemically attached onto many other metals,[14] indicate that judicious connection of various DNA-modified carbon nanotubes with the large varieties of nanoparticles grafted by DNA chains of complimentary sequences should lead to the formation of many multinanotube multicomponent assemblies. The structure of the self-assemblies thus formed can be, in principle, regulated by modifying single nanotube ends with ssDNA chains of different base sequences and/or controlling the number of cDNA chains grafted onto each of the nanoparticles.

In conclusion, we have demonstrated that a wide range of multicomponent structures of carbon nanotubes can be constructed by DNA-directed self-assembling of carbon nanotubes and gold nanoparticles. In view of the availability of various carbon nanotubes of different structures and DNA chains of different base sequences, the work presented here represents an important advance in constructing many multiple carbon nanotube self-assembled structures for multifunctional material and device applications.

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