Communication

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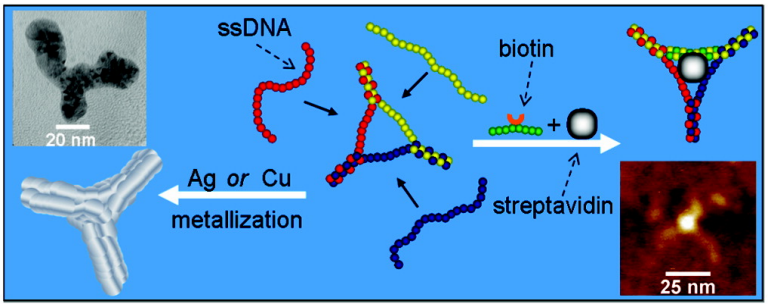

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DNA-Templated Three-Branched Nanostructures for Nanoelectronic Devices

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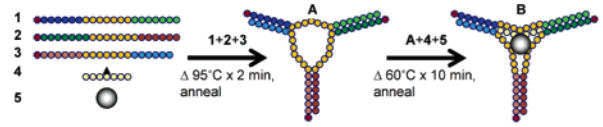
DNA-templated nanofabrication is an attractive approach for the self-assembly of nanoelectronics, and a number of advances have been achieved in this field.[1,2] Double-stranded (ds) DNA has served as template for the deposition of conductive materials, including silver,[3] palladium,[4] copper,[5] and carbon nanotubes.[6,7] Single-stranded (ss) DNA has also been demonstrated as a template for silver metallization.[8] The electrical conductivity of dsDNA-templated nanowires has been characterized.[3,4] Sequence-specific metallization of DNA[9,10] has allowed the construction of a substrate-gated, DNA-templated field effect transistor.[7] Indeed, the linear nature of DNA makes it well suited for the fabrication of two-terminal nanoelectronic devices; however, greatly increased flexibility in device design could be achieved through nonlinear, branched DNA structures. In this regard, Seeman and co-workers have provided elegant examples of the construction of complex two-dimensional arrays from DNA,[2,11] but isolated branched DNA structures for nanoelectronic devices have not been demonstrated. In this Communication, we report the use of DNA templating for the fabrication of *discrete* three-branched metal nanostructures as precursors for three-terminal nanoelectronic devices. These DNA-templated entities, along with other branched nanostructures,[12] should provide a path to the construction and detailed electrical characterization of individually gated nanodevices, which are desirable in achieving electrical signal gain and independent device operation.[13]

Our approach (Scheme 1) begins with the design of three oligonucleotides (**1**−**3**) that self-assemble into a three-branched motif (complex **A**). The arms of the complex have stable dsDNA portions and sticky-end overhangs to facilitate manipulation and/or extension. The core of the assembly is a ssDNA region designed to facilitate directed hybridization of a biotinylated oligonucleotide (**4**), which can be tagged with streptavidin (**5**) to give complex **B**. Oligonucleotide sequences were selected using in-house-written software that generates a ssDNA sequence and checks it for primer−dimer complexes, minimizing their length and melting temperature (see Supporting Information).

Oligonucleotide reaction mixtures were deposited on mica surfaces and imaged by atomic force microscopy (AFM). Figure 1A−C shows representative images of discrete and well-defined three-branched DNA structures (**A** in Scheme 1). Substrates having the streptavidin-tagged three-armed assemblies provided AFM data (Figure 1D−F) consistent with complex **B** in Scheme 1. The expected arm length in structures **A** and **B** was ∼21 nm; the mean arm length in 40 complexes was 26 nm with a standard deviation of 5 nm. The slightly greater AFM lengths are likely due to tip convolution (see Supporting Information). Importantly, the ability to (1) assemble these complexes in solution with potentially high yields (∼50%; see Figure S-3 in Supporting Information) and (2) specifically localize nanostructures using straightforward biotin streptavidin chemistry should be valuable for the bottom-up self-assembly of materials that could potentially form nanoelectronic devices.

Scheme 1. Assembly and Specific Labeling of a Three-Branched DNA Complex[a]



[a] Oligonucleotides **1**, **2**, and **3**: long (∼120 base) oligonucleotides with complementary regions represented as tonal variations of the same color (i.e., dark vs light green). **4**: Internally biotinylated poly-T sequence, complementary to the dark yellow regions in **1**−**3**. **5**: Streptavidin. **A**: Three-branched DNA nanostructure assembly. **B**: Streptavidin-labeled, three-armed DNA complex.

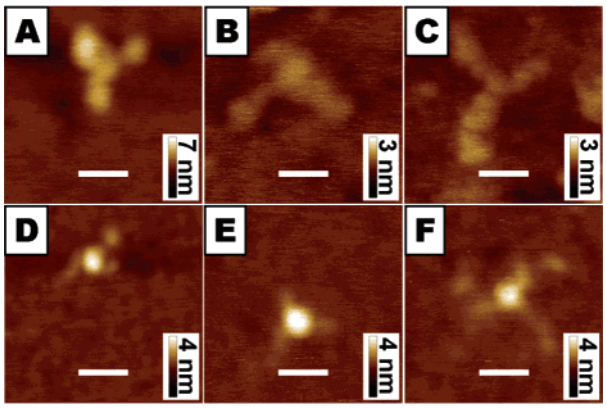


Figure 1. Tapping mode AFM height images of structure **A** (A−C) and of structure **B** (D−F) on mica surfaces. The presence of a globular raised region at the center of each complex **B** is evident. The white bar represents 25 nm in all images.

Depositing conductive material around nucleic acids is an essential step in the production of DNA-templated nanoelectronic devices. In this work, we demonstrate highly specific metallization of branched DNA complexes using both silver[3,8] and copper.[5,8] Figure 2A−D displays transmission electron microscopy (TEM) images of complex **A** after silver metallization, in comparison to a silver-metallized control substrate that lacked DNA (Figure 2E). The seeding and templating effect that the DNA exerts on the deposition of silver is manifested clearly. On the DNA-containing surfaces, the shape of the metallized features resembled DNA complex **A**, whereas control surfaces only showed much larger silver deposits with irregular shapes. Furthermore, we found that the pH of the reducing solution influenced the degree of polycrystallinity of the metallized complexes. At higher reducing solution pH (8−12), primarily polycrystalline silver nanostructures were formed (Figure 2A), while at lower reducing solution pH (2−

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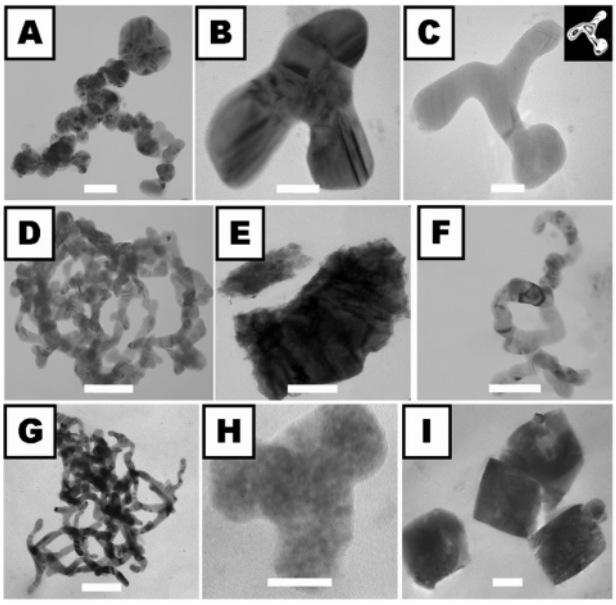

Figure 2. TEM images of DNA-templated metallization of complex **A** with silver (A−E) or copper (F−I), on carbon-coated TEM grids. (A) Polycrystalline structure with multiple grains that extend well beyond the DNA template. Scale bar is 50 nm. (B−C) Nearly single-crystalline metallized complexes with dimensions closer to those of the DNA template show fewer crystal defects and grain boundaries. Scale bars are 25 nm. (C) Inset is a dark-field TEM image. (D) Higher-order cluster of DNA-templated silver nanostructures showing multiple filamentous features that branch at regular intervals. The white bar depicts 100 nm. (E) Micron-scale silver crystals with irregular features on a control grid containing no DNA. Scale bar is 2 μm. (F) Lower- and (G) higher-order clusters of crystalline DNA-templated copper metallization products. Scale bars are 50 and 100 nm, respectively. (H) More abundant, three-branched polycrystalline copper nanostructures. Scale bar is 25 nm. (I) Control experiments on surfaces lacking DNA complexes show large copper crystals. Scale bar is 100 nm.

6), DNA-templated silver products were more single crystalline (Figure 2B,C). Indeed, dark-field TEM images of complex **A** metallized with reducing solutions at lower pH values indicate the nearly single-crystallinity of some of the resulting structures (Figure 2C, inset). The substrate also influenced the morphology of the DNA templates, which sometimes formed higher-order clusters on hydrophobic TEM grids, compared to primarily isolated three-branched complexes on mica. When these clusters were metallized, they formed seemingly interwoven bundles of DNA-templated silver branching at regular intervals, as shown in Figure 2D. Preferential axial extension of branches (e.g., Figure 2C) may be due to the deposition kinetics for the different crystalline planes, although further studies will be needed to elaborate the mechanism more fully.

Metallization of three-branched DNA assemblies with copper was also highly specific. Complex **A** was formed and deposited on TEM grids, and then metallized with copper.[14] TEM analysis revealed clear differences between copper-metallized surfaces containing DNA templates (Figure 2F−H) and metallized control substrates lacking DNA templates (Figure 2I). A few clusters of more highly crystalline, branched copper nanostructures were identifiable (Figures 2F,G), but more commonly, we observed polycrystalline metallization of individual DNA complexes (Figure 2H). Metallization under milder conditions should favor the formation of structures whose features are more single crystalline, as we have observed for silver. We have also characterized metallization products of complex **B**, but the thickness of metal deposition necessary for TEM analysis obscures the low-contrast streptavidin core.

Nanometer-resolution energy-dispersive X-ray (EDX) studies on metallized nanostructures were carried out with a scanning transmission electron microscope. On silver-metallized DNA templates, Ag_L X-rays were the most intense of the bands not arising from the grid, revealing that the studied clusters were mainly composed of silver (see Supporting Information, Figure S-8). Moreover, EDX analysis of copper-metallized complex **A** showed a Cu_L peak signal strongly correlated with the morphology of the structure (see Supporting Information, Figure S-9), indicative of DNA-templated three-branched copper deposits.

In conclusion, we have demonstrated the design, self-assembly, and specific metallization of a three-branched DNA motif that can be specifically labeled at the center using biotin−streptavidin coupling. The formation of complexes, both with and without conjugated streptavidin, has been established by AFM. Moreover, silver and copper metallization of these complexes with high specificity for the DNA template has been achieved. Electron microscopy analysis of these DNA-templated nanostructures has revealed their morphology, and high-spatial-resolution EDX of the metallized products has confirmed their composition. Rationally designed three-armed DNA complexes could potentially serve as positioning and connecting tools for streptavidin-tagged semiconductor nanocrystals or other electronically active nanomaterials, thus providing a novel means for the construction of multiple, independently operable three-terminal nanoelectronic devices. These results indicate promising potential for the use of three-branched DNA complexes in the bottom-up self-assembly of nanoelectronics.

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Supporting Information Available: Experimental details, statistical analyses, instrumental conditions, AFM images, and EDX data. This material is available free of charge via the Internet at http://pubs.acs.org.

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