Assembly of Nanoelectronic Components by DNA Scaffolding

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The development of electronic circuitry based on nanoparticles, molecules, and other nanoscale devices will require a major paradigm shift involving circuit architecture, device principles, and fabrication technologies. Due to basic design constraints imposed by power dissipation limits and the interconnect bottleneck, nanoscale circuitry will be dominated by ultrasmall components laid out in regular patterns and connected locally [1,2]. The realization of such circuitry will require a radically new method for precision assembly of nanocomponents into regular arrays. In this project, we are investigating the use of DNA as a scaffolding for the programmed assembly of nanoelectronic component arrays.

An example of the assembly of a nanocomponent array by DNA scaffolding is illustrated schematically in Fig. 1. Rather than using the lithographic techniques of conventional semiconductor chip manufacturing, this approach exploits programmed Watson-Crick base-pairing for self-assembly at the nanoscale. In this design, the base sequences for 22 different types of single-stranded DNA are programmed so that a mixture of strands self-assembles into tiles comprised of double-crossover (DX) molecules (represented by 5-color cells in Fig. 1), which in turn assemble into a two-dimensional crystal. Nanoparticles, or other nanoscale components, are assembled into the scaffolding by covalent attachment of the particles to one type of DNA strand, thereby offering a precision limited only by the 0.34-nm nucleotide separation of the DNA duplex.

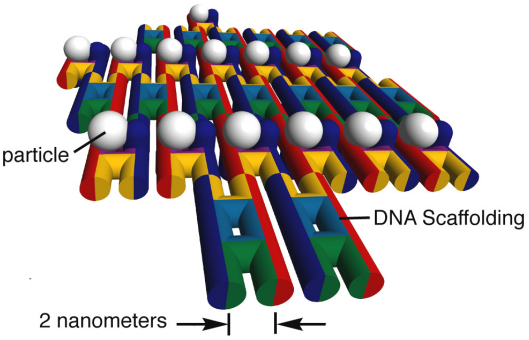

Fig. 1. Schematic diagram illustrating the programmed assembly of nanoparticles along attachment lines on a DNA scaffolding. Colored segments represent DNA strands that self-assemble into molecular tiles which form a two-dimensional structure. Particles and other nanocomponents precisely attach to the scaffolding along lines by Watson-Crick base pairing.

The goal of this project is to identify and address basic scientific and engineering challenges toward proof of concept for this approach. Our team from electrical and computer engineering, chemistry, and physics is carrying out a range of studies to systematically explore basic chemical, physical, and electronic issues related to nanoparticle/DNA design, chemical compatibility, assembly methods, electrostatic interactions, electronic transport, and interactions with surfaces. This research will help lay the groundwork for the development of a DNA nanotechnology for the precise assembly of components for electronics and other applications.

Prior work by members of our team demonstrated [3] the assembly of 1.4-nm gold nanoparticles by the design shown schematically in Fig. 2. The DNA scaffolding was formed by the assembly of a set of 22 specifically designed synthetic oligonucleotides in solution. The strands form four types of DX molecules, referred to as A,B,C,D in Fig. 2. Molecules B and D are designed to have structural features protruding perpendicular to the crystal plane. One of the protruding structures in the B molecule is exploited to incorporate nanoparticles into the crystal. The four types of DX molecules are designed to self-assemble by sticky-ended cohesion so as to tile the plane, thereby forming the two-dimensional crystal. The spacing between the B and D molecules in the crystal is 32 nm, while the spacing between identical molecules (A-A, B-B, etc.) in the perpendicular direction is 4 nm.

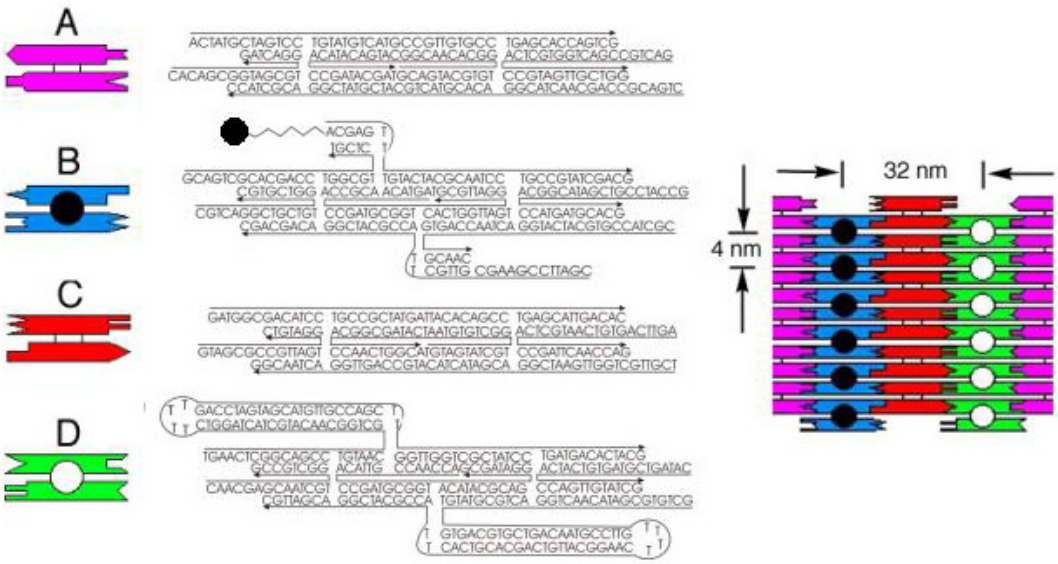

Fig. 2. Base sequences of the four DX molecules (A-D) and the tiling pattern used to assemble the 2-dimensional DNA crystals reported in Ref. [3]. The sequences of the 22 DNA strands including the DNA-Au conjugate (35-mer present in tile B; covalently attached gold nanoparticle indicated by a filled circle) are shown along with symbolic representations to the left. Molecules B and D each contain two protruding structures that extend out of the crystal plane, one above and one below the plane. The open and filled circles in the figure represent the protruding structures on one side (e.g., above) the plane. In the final DNA assembly shown at the far right, the spacing between these features is 32 nm in the horizontal direction and 4 nm in the vertical direction.

The Au nanoparticle used in this study is comprised of a Au_{55} cluster passivated with a phosphine ligand shell that is functionalized with a single reactive maleimide group. DNA-Au conjugates were formed by covalently attaching this particle to the 5' end of a thiol-containing DNA oligonucleotide that is part of one of the protruding structures of tile B. The design in Fig. 2 allows the assembly of particles along lines in the scaffolding spaced 64-nm apart by the incorporation of the DNA-Au conjugate into the scaffolding during crystal growth.

A darkfield scanning tunneling electron microscope image of a DNA crystal prepared by the above method is shown in Fig. 3. The figure shows that Au nanoparticles have been assembled into the DNA crystal along lines that are approximately 64 nm apart, consistent with the scaffolding design. While distinct DNA features are discernable in the structure midway

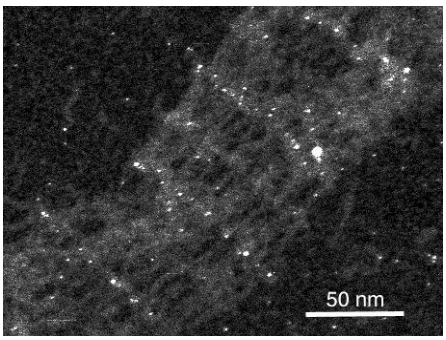

Fig. 3. Scanning transmission electron microscopy image showing the assembly of 1.4-nm Au particles by DNA scaffolding by the scheme illustrated in Fig. 1. (From Ref. 3)

between the lines of Au nanoparticles, no significant attachment of Au is observed at the midway points. This is consistent with the alternation of Au-decorated (B) molecules and undecorated (D) molecules in the design.

These previously reported results provide a preliminary demonstration of nanocomponent assembly by DNA scaffolding. However, considerable improvement is necessary to demonstrate the usefulness of this approach as a manufacturing technology. In particular, the size of the DNA crystal shown in Fig. 3 is small and its quality is poor. Hence, a goal of our recent work has been to realize precision assembly for large, high-quality crystals by improvement in the DNA-Au conjugate design and the assembly scheme. Recently, an important step was demonstrated. As shown by the high-resolution atomic force microscopy image in Fig. 4, gold nanoparticles have been precisely aligned along DNA attachment lines midway between particle-free DNA markers in a large, high-quality DNA scaffolding. These results suggest that the next major goal for this study – the precision assembly of closely spaced nanoparticles in long, linear arrays – is within reach.

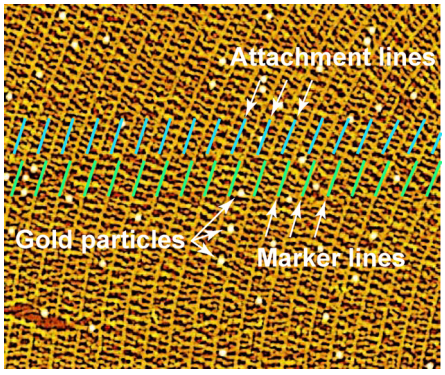

Fig. 4. Atomic force microscopy image demonstrating precision assembly of gold nanoparticles along attachment lines on a high-quality DNA scaffolding. DNA marker lines have a similar structure to the DNA attachment lines but are designed to remain particle-free. (Blue and green segments indicate line positions. Markers are 64 nanometers apart.)

Additional steps toward demonstrating the feasibility of assembling electronic circuitry by this approach have also been recently demonstrated by our team. These include basic studies of the aggregation of charged colloids [4], which will help to build a fundamental understanding of charging effects in DNA-particle mixtures, and the study of the electrical characteristics of alkanethiol and oligo(phenylene-ethynylene) molecules [5], which will be useful for the design of molecular components for the demonstration of electronic function in DNA-assembled nanoelectronic arrays.

References

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[2] T. Yang, R. A. Kiehl, L. O. Chua, "Tunneling phase logic cellular nonlinear networks," Intl. Journal of Bifurcation and Chaos, Vol. 11, pp. 2895-2912, December 2001
[3] S. Xiao, F. Liu, A. E. Rosen, J. F. Hainfeld, N. C. Seeman, K. Musier-Forsyth, and R. A. Kiehl, "Self-assembly of metallic nanoparticle arrays by DNA scaffolding," J. Nanoparticle Research, Vol. 4, No. 4, pp. 313-317, August 2002.
[4] R. Zhang and B. I. Shklovskii, "Phase diagram of aggregation of oppositely charged colloids in salty water," submitted for publication.
[5] J. D. Le, Y. He, C. C. Mead, T. R. Hoye and R. A. Kiehl, "Negative differential resistance in a bilayer molecular junction," Appl. Phys. Lett., to be published Dec. 2003.