Programmed Assembly of Quantum-Dot Arrays on DNA Templates: Hardware for Quantum Computing?

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Abstract: This paper reports progress in the fabrication and characterization of an array of 1nm-scale colloidal particles (i.e., quantum-dot array) that can be operated to execute nontrivial and innovative computations, possibly including quantum logic. We discuss the actual fabrication of 2-nm metal clusters as an example of possible quantum dot implementation. Innovative and unconventional paradigms underlie the different stages of this work. For example, regular array geometry is achieved by directing appropriately derivatized metal clusters to preselected locations along a stretched strand of an engineered DNA sequence.

OCIS Codes: (160.2100) Electro-optical materials; (160.4330) Nonlinear optical materials

1. Introduction

The proposals for the physical implementations of quantum computation span virtually every branch of quantum physics (e.g., see [1]). Many of these proposals have been motivated by recent advances in nanoscale science and engineering, including, in particular, quantum dots and quantum-dot arrays (e.g., see [2-4]). An approach to quantum computing that has not received broad attention is that of the quantum implementation of the cellular automaton [1]. As Lloyd has indicated in his original work [5], arrays of weakly coupled quantum systems can be made to compute by subjecting them to a sequence of electromagnetic pulses of well-defined frequency and length, and programming such computers is accomplished by selecting the proper sequence of pulses. Local control of the qubits is not required. New theoretical work by Benjamin shows how relatively simple local rules would permit the implementation of some quantum computations [6]. This work points toward the fabrication of an array of quantum-confined electron systems that can be addressed globally in a spectroscopic fashion.

In this context, we report progress [7] in the development and characterization regular arrays of nanometer-sized colloidal clusters (e.g., Au, Ag, and Pt). Regular array geometry is achieved by directing appropriately derivatized metal clusters to preselected locations along a stretched strand of an engineered DNA sequence. We are interested in exploring these interesting nanoscale systems for possible implementations of quantum logic.

2. Programmed assembly of nanoparticles

The ability to assemble nanoparticles in a precise and controlled way is key to the fabrication of a variety of nanodevices. Networks of nanometer–sized metal or semiconductor islands, or quantum dots, may exhibit a variety of quantum phenomena, with applications in optical devices [8], nanometer-sized sensors [9], advanced computer architectures [10,11], ultra dense memories [12], and quantum-information science and technology [1]. The challenge is that fabrication of nanoparticle arrays in a time and cost effective manner remains a formidable task. Particle-based and e-beam lithography lack the required resolution. Scanning probe microscopy can be used for making molecular devices, but it is slow and impractical for mass production. A variety of other techniques have been demonstrated, including self-assembled monolayers [13], block copolymer template lithography [14] or electro deposition [15], and controlled deposition by cleaved edge overgrowth [16]. All of these techniques have limitations on the size of the particle and/or the pattern of the resulting array.

Interest in the concept of self-assembled nanostructures led to the idea of using DNA as a scaffold or template for the programmed assembly of nanoscale arrays (see review by Storhoff and Mirkin [17]). Beginning in the 1980s Seeman *et al*. experimented with combining DNA fragments to produce geometrical shapes, including cubes [18], triangles [19], two-dimensional arrays [20,21,22] and various forms of DNA knots [23,24]. Using DNA as a structural molecule has many advantages. It can be easily synthesized in lengths up to 40 nm and double-stranded DNA can be joined end to end to produce longer linear molecules or more complex shapes. It can be modified with functional groups at predetermined sites to allow for the attachment of other molecules in a specific manner.

DNA has been used previously in the programmed assembly of particles**.** Mirkin *et al*. [25,26,27] and Alivisatos *et al.* [29,30] have successfully attached oligonucleotide-derivatized nanoparticles to DNA using hybridization techniques. Alivisatos also bound gold particles to both single-stranded and double-stranded DNA modified with

thiol groups [23]. Niemeyer and coworkers conjugated streptavidin to single-stranded DNA oligonucleotides, hybridized the conjugates to a complementary RNA template, and bound biotinylated gold clusters to the streptavidin [31]. Cassell *et al.* assembled fullerene derivatives along the phosphate groups of the DNA backbone using cation exchange [32] and Coffer and coworkers formed rings of cadmium sulfide nanoparticles using double-stranded circular plasmid DNA attached to a solid substrate [33].

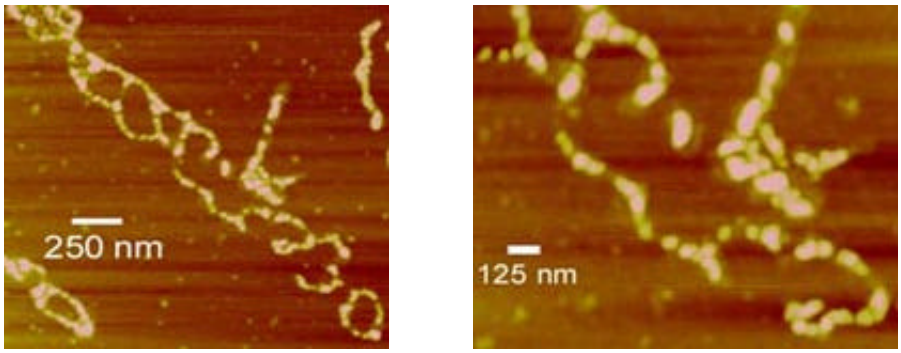

Figure 1. AFM images of gold nanoparticles bound to DNA. **a.** Carboxylic acid functionalized gold particles bound to amino-modified thymines on DNA in the presence of methylamine. **b.** Close-up view showing DNA between gold particles.

In what follows, we describe our work [7] in the programmed assembly of functionalized nanoparticles to chemically modified bases on double-stranded DNA. This method of nanoparticle assembly would potentially allow closer spacing of very small particles than hybridization based methods. It would also allow greater precision in the placement of particles than using a plasmid or the DNA backbone as a template.

Oligonucleotides were designed with amino-modified bases for attachment to carboxylic acid functionalized gold particles. The modified bases were separated by approximately 3.7 nm (11 base pairs). Gold nanoparticles with an average diameter of 1.5 nm were synthesized with a mercaptosuccinic acid coating [34]. Each particle has multiple reactive carboxyl groups on its surface. In order to decrease the chances of one particle binding to many amino groups on the DNA, an agent was used to block some of the carboxyl groups on the gold. Methylamine was chosen because of its small size and similarity to the methylene side chain containing the amino group on the DNA. Analysis of the products by transmission electron microscopy (TEM), and atomic force microscopy (AFM) showed the gold particles bound to the DNA.

In the process of binding the DNA and gold nanoparticles without the competition from the methylamine blocker, the gold particles are bound to the DNA but multiple strands of DNA are held together because of the many reactive sites on each gold particle. The particles cause cross-linking between different DNA strands and possibly between different sites on the same DNA strand, leading to an aggregate of DNA and gold. Figure 2 shows AFM images of DNA bound to gold in the presence of methylamine. The methylamine concentration in the reaction was equal to twice the concentration of amino-modified thymines on the DNA. Figure 2a shows double-stranded DNA bound to gold nanoparticles with greatly reduced cross-linking compared to a reaction without methylamine. Figure 2b shows a close-up of a portion of 2b with the DNA between gold particles clearly visible between the gold clusters. Sectional analysis of a strand of DNA bound to gold shows the gold particles are separated by multiples of the 3.7 nm between binding sites. The closest particles in this image are approximately 18 nm apart, separated by 5 binding sites on the DNA. It is unclear why some binding sites are not occupied. Further studies are underway to address this issue.

The advantages of this method are that nanoparticles can potentially be placed wherever a modified base is inserted during synthesis of the DNA. Bases are separated by about 0.34 nm in a DNA double strand, allowing the placement of particles with sub nanometer precision. Therefore, arrangement of the particles is dependent only on design of the DNA template and the size of the particle. A variety of functional groups can be used to modify DNA during synthesis and any particle that can be functionalized with a complementary reactive group can be bound to the DNA. The DNA product is double-stranded thus retaining the regularity of structure that makes DNA an attractive template for nanofabrication and assembly of nanoparticles. In summary, this technique satisfies a basic need to assemble one-nanometer-scale objects in a programmable manner and in a massively parallel fashion, from the bottom up.

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