

Chains of semiconductor nanoparticles templated on DNA

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Towards the construction of DNA templated nanowires for self-assembled nanodevices, nanocrystals of the *p*-type semiconductor CuS were grown selectively and densely on DNA both in solution and stretched on a surface. Atomic force microscopy and transmission electron microscopy measurements display chains of CuS nanoparticles up to 10 nm diameter separated by less than 40 nm. By increasing the number of nucleation sites through the use of bundles of DNA, highly dense coverage of the DNA with nanocrystals is observed. © 2004 American Institute of Physics. [DOI: 10.1063/1.1775884]

At molecular scales (<10 nm), the breakdown of conventional bulk physical processes poses a challenge for the creation of useful nanoelectronic devices from nanoscale and molecular building blocks. Furthermore, a major challenge in assembling devices from nanoscale objects is the lack of adequate tools and procedures for (i) manipulating and positioning these small objects and (ii) establishing electrical contact to the macroscopic circuitry. Biological molecules such as DNA have undergone extensive evolution to enable self-assembly to take place with high specificity and with mechanisms for error correction. Simple Watson-Crick base pairing allows DNA to behave in a deterministic way that enables even complex, seemingly unnatural structures, such as two-dimensional lattices and DNA nanomachines, to be constructed.^{1,2} However, DNA itself has limited use as the active component in electronic devices because the balance of evidence suggests that DNA is insulating,^{3–6} except in special cases of short strands (<10 nm) with specific sequences.^{7–9} One strategy to overcome this electrical inactivity of DNA but to still take advantage of the self-assembly properties, is to use the molecule as a template for the growth of metals^{10–13} and semiconductors.¹⁴

An example of the self-assembly and subsequent mineralization of DNA in an electronic structure was demonstrated by Braun and co-workers.¹⁰ They hybridized λ -DNA with complementary oligonucleotides attached to gold electrodes to create a single bridge spanning a gap of 12–16 μm . The DNA was then used as a template for the directed synthesis of chains of silver nanoclusters from silver ions to produce a conducting nanowire. The corresponding current–voltage measurements indicate ohmic behavior with conductivities close to the bulk metal. It is envisaged that with the correct selection of oligonucleotides, multiple DNA–DNA junctions contacted to an array of electrodes can be used to template standard semiconductor junctions (such as *p*–*n*, bipolar junction transistor, and logic junctions) using self-assembly and the directed growth of semiconductor on DNA. However, chemistry on DNA has been mainly limited to the reduction of metal ions (for example, Ag, Au, Pd, and Pt) along the molecule. Growing a semiconductor densely along DNA to create a semiconducting nanowire remains a challenge. In this work, we demonstrate the dense growth of nanoparticles

of the *p*-type semiconductor copper sulfide on DNA functioning as a selective template both in solution and on a surface.

Copper sulfide (CuS) is a semiconductor with the mineral structure covellite, which has an indirect bandgap of 1.55 eV.¹⁵ We template the growth of CuS with DNA using two methods: the first is in solution and the second on DNA immobilized on a surface. With the first method, lambda phage DNA with an approximate length of 16 μm (48 502 base pairs) was incubated with an equimolar concentration of CuCl₂ (0.2 mM) for 20 min, after which a stoichiometric solution of Na₂S was added. An absorption spectrum taken of the solution of mineralized DNA exhibits the characteristic absorption onset of CuS as well as the signature absorption

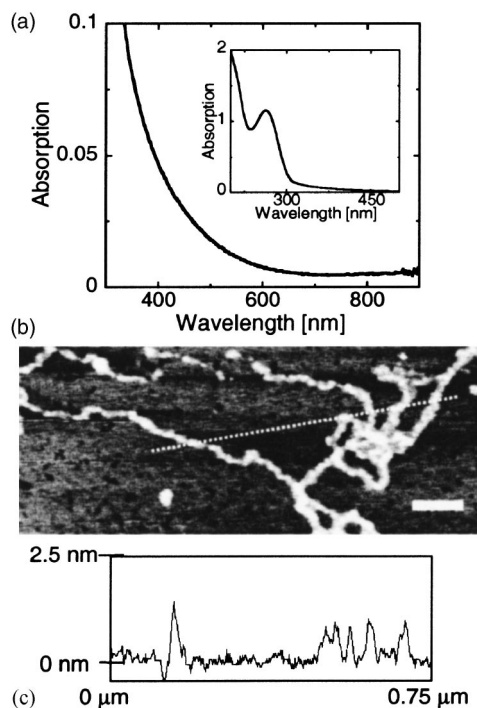


FIG. 1. (a) Absorption spectrum of the solution containing the CuS-DNA hybrid showing CuS absorption. The inset displays the DNA absorption peak at 260 nm for the sample. (b) Topographic AFM image of λ -DNA coated with CuS nanoparticles on mica. The scan area is 1 μm and the scale bar shown is 100 nm. (c) Cross section of the area indicated by a dotted line in (b). The average nanoparticle height is approximately 1.2 nm.

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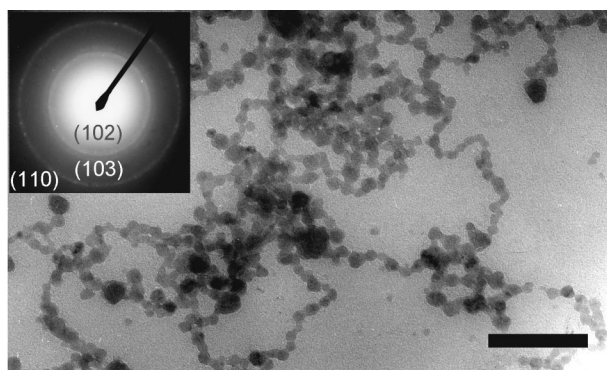


FIG. 2. TEM of CuS nanocrystals grown along DNA immobilized on a surface. The scale bar is 100 nm. The inset displays the electron diffraction pattern of a 3 μm area with the indexed reflections corresponding to the covellite structure of CuS.

peak of DNA at 260 nm [Fig. 1(a)]. The weak absorption and slow onset is consistent with the indirect bandgap of CuS. A small drop of the solution was spread on a mica substrate using spin coating, and atomic force microscopy (AFM) was subsequently performed in the tapping mode. Figure 1(b) displays a DNA strand covered densely with CuS nanoparticles and very few individual particles in the background. The entire structure, consisting of CuS nanoparticles and DNA, has a combined average height of 1.2 nm. We find that native DNA, imaged on a mica substrate using a silicon probe tip, has a height of 0.3 nm [see Fig. 3(a)], which is consistent with values measured by other groups.^{16,17} The dense growth of CuS selectively on DNA is due to the strong binding of Cu^{II} to the phosphate backbone and bases of DNA.¹⁸ The template serves to locally increase the concentration of Cu^{II} and enhance nucleation. The CuS-DNA wire structure is stable to flocculation and the strand can be easily positioned and stretched, using standard molecular combing methods,¹⁹ between electrodes.

In order to generate electronic devices from junctions formed by DNA contacted to electrodes, it is also important to be able to synthesize a semiconductor along DNA immobilized on a surface.

Elongated λ -DNA was obtained either through molecular combing on silicon or spin casting on mica. The immobilized DNA sample was pretreated by incubating in a concentrated solution of CuCl_2 (5 mM) to permit exchange of the sodium counterions in DNA with copper ions, after which excess copper ions were removed by thorough washing with water and drying. The sample was then submerged in a dilute solution of CuCl_2 (0.2 mM) and H_2S was slowly bubbled through for 1 h. As seen in Figs. 2 and 3(b), CuS nanoparticles preferentially nucleate and grow along the DNA strand. The particles prepared by this method are separated by less than 40 nm have heights as large as 10 nm, which is larger than those resulting from the first method. We use transmission electron microscopy (TEM) to verify the identity of the nanoparticles and probe their crystallinity. The TEM sample was generated by evaporating a layer of carbon onto the mica sample that holds the CuS-coated DNA, then floating the carbon film in water and picking it up with copper grids. The carbon film that delaminates contains the CuS-coated DNA (Fig. 2). The electron diffraction pattern of the CuS-DNA hybrid exhibits clear reflections from the individual nanocrystals, which form noncontinuous rings cor-

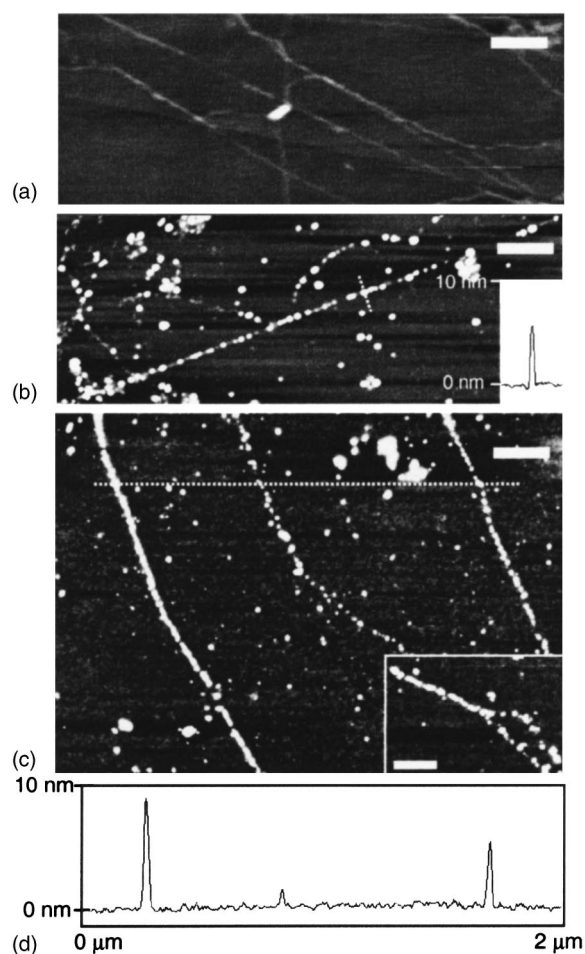


FIG. 3. Topographic AFM images of (a) λ -DNA stretched on mica using a spin coating technique. The average height of one strand is 0.3 nm. (b) DNA coated with CuS nanoparticles on mica. The inset displays a cross section of the area indicated by a dotted line for a nanoparticle with 6 nm height. (c) CuS nanowires comprising of nanoparticles grown along stretched bundles of DNA on silicon. The inset of (c) is of a scan area of 700 nm and displays CuS-coated DNA bundle at a branch point. The bundle has denser CuS coverage than the individual strands. (d) Cross section of the area indicated by a dotted line in (c). The scan area for the large image is 2 μm , and all scale bars are 200 nm. Images have a height scale of 5 nm.

responding to the (102), (103), and (110) directions of the CuS covellite crystal lattice (Fig. 2 inset). The copper sulfides are a particularly interesting system because of the range of stable and metastable crystalline phases, with varying electrical properties, that are accessible starting from covellite by thermal annealing between 100 and 400 $^{\circ}\text{C}$.^{15,20} Through careful control of the annealing conditions, it is possible between 300 and 400 $^{\circ}\text{C}$ to obtain the djurleite phase, which has a direct bandgap.¹⁵ Post-growth high temperature heat treatment of continuous chains of CuS nanoparticles on DNA can be employed to potentially obtain nanowires with a range of electronic properties.

For the construction of a nanowire that can conduct current, it is necessary to further improve nucleation. We can increase the number of nucleation sites for CuS by using bundles of DNA, which develop during molecular combing on silicon. The density of copper sulfide particles grown on these bundles increases with the number of strands in the bundle [Fig. 3(c)]. This difference in nanoparticle density is easily seen in the inset of Fig. 3(c), in which a bundle branches into individual strands. The higher number of

strands results in a larger density of binding sites for copper ions and thus more nucleation sites are available for the growth of a more continuous CuS semiconductor nanowire. Work is currently underway to attach these nanowires to electrodes and to determine their electrical properties. Although bundles formed from molecular combing are difficult to control, bundles of DNA of a defined strand number can be generated from crossover junctions.^{21,22} Such bundles can also have defined sticky-ends, which are able to self-assemble at electrodes. Some of the advantages of the methods described in this work over the other report of semiconductor growth on DNA¹⁴ are the flexibility afforded by the possibility of both solution and surfaced-based techniques and the absence of a bulky, insulating ligand to mediate the synthesis that can hinder proper contact to electrodes, making it difficult for use in device applications.

In conclusion, we have shown that DNA can be used as a specific template for the dense growth of nanoparticles of the *p*-type semiconductor CuS both in solution and on a substrate. The nanoparticle size ranges from 1 to 10 nm, with the larger crystalline particles grown on DNA first immobilized on a substrate. Higher density growth results when bundles of DNA are used as a template for the semiconductor. The ability to grow various semiconductors on DNA allows the combination of solution-based self-assembly of DNA with the superior electronic properties of inorganic semiconductors in the fabrication of nanoelectronic devices.

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