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14. ABSTRACT In this project, the PIs have successfully demonstrated several methods for controlled assembly of inorganic nanostructures based on chemical and biochemical techniques. These results include: – electroless metallization of DNA to form nanowire interconnects; – lithographic modification of the surface chemistry to create patterns for attachment of DNA and metallic nanoparticles;					
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Single-Electron Transistors Templated on Self-Assembled DNA Scaffolds

By: Gleb Finkelstein and Thomas H LaBean.

In this project, the PIs have successfully demonstrated several methods for controlled assembly of inorganic nanostructures based on chemical and biochemical techniques. These results include:

- electroless metallization of DNA to form nanowire interconnects;
- lithographic modification of the surface chemistry to create patterns for attachment of DNA and metallic nanoparticles;
- single electron transistors based on individual nanoparticles;
- control of length and directionality of DNA superstructures by incorporation of double strand DNA bridges in stepwise assembly processes.

These topics are discussed in greater details below:

DNA metallization

To fabricate conductive interconnects, we have developed a novel *electroless* (i.e. without electrical current) deposition technique to metallize DNA in solution [1]. We coated double-stranded DNA molecules, both synthetic and natural, in both silver and gold. Figure 1a shows silver nanowires imaged by the Scanning Electron Microscope (SEM). The metallized DNAs have diameters down to 15 nm, which makes them almost an order of magnitude thinner than the previous DNA or protein-based metal wires (~100 nm) [2-8], and among the thinnest metal wires available to date by any method. Our nanowires are easily reproducible and have negligible granularity, as visualized by SEM and TEM. The wires have been contacted by leads formed by e-beam lithography (Figure 1b) and show resistances in the range of 200-1000 Ohm. This resistance is dramatically lower compared to previously reported double-helix DNA templated silver nanowires [2]. The resistance drops even further at liquid nitrogen temperature, which indicates the high intrinsic quality of the wire material (Figure 1c).

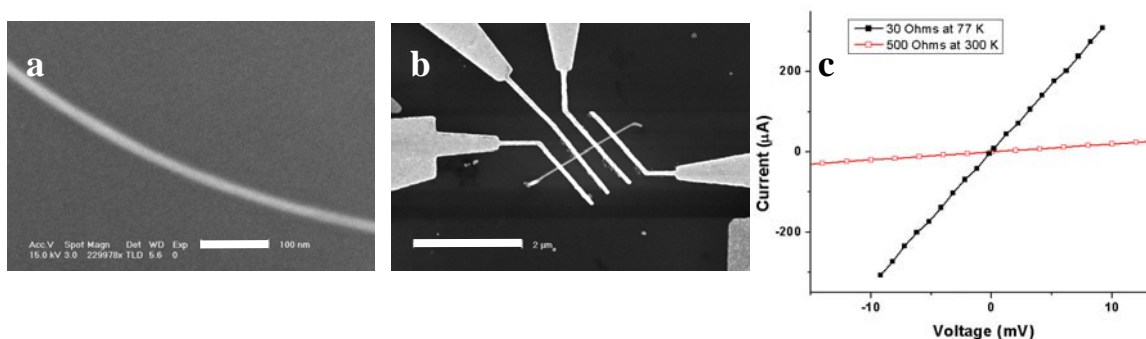


Figure 1. SEM images of a 15-nm wide metallized DNA molecule (a) with a number of contacts fabricated by e-beam lithography (b). Scale bars: a) 100 nm and b) 2 microns. (c) I(V) curves measured on one of the metallized DNA molecules at room temperature and at liquid N₂ (77 K). The resistance is much lower at low temperature, which indicates a high intrinsic quality of the wire material.

Chemical surface patterning for selective attachment

One of the challenges in fabricating SETs based on metallic nanoparticles is to ensure the correct placement of nanoparticles and nanoparticle assemblies on the substrate. By selectively depositing particles, it should become possible to significantly increase the yield of functional devices. We have recently developed a technique to attract gold nanoparticles at chemically functionalized locations on the SiO₂ surface [9]. We define the desired pattern on the surface by e-beam lithography and treat it with APTES (3-aminopropyltriethoxysilane). APTES covalently attaches to the surface and displays positively charged amine groups. These groups in turn attract the negatively charged citrate-stabilized colloidal gold nanoparticles [10, 11]. A similar method was recently applied to the DNA, which is also negatively charged [12].

In Figure 2a we demonstrate high deposition specificity and good surface coverage achieved by our chemical patterning method. Varying the parameters, it is fairly straightforward to deposit particles in single file, zigzag or double lines (Figure 2b). Using e-beam lithography, we deposited pairs of contacts on top of the nanoparticles (Figure 2c) to probe their electrical conductance (see discussion in the next section). Finally, we conducted an experiment where the surface was patterned successively with horizontal lines of 13 nm particles and then with vertical lines of 50 nm particles. We find that the particle attachment to the surface is rather strong: the 13 nm particles stayed on the surface through the second patterning stage and deposition of 50 nm particles [9].

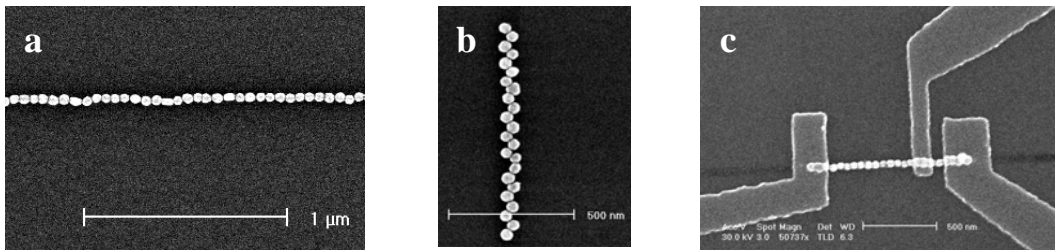


Figure 2. a) Gold nanoparticles are selectively deposited on the surface along a patterned line. b) By controlling the parameters of the pattern, more complex structures are achieved. c) Contacts are made by e-beam lithography to the nanoparticle array and to a single nanoparticle.

Functional SETs made by NP attachment

Linear nanoparticle arrays, such as shown in Figure 2, already greatly facilitate the fabrication of functional SETs from one or several interconnected nanoparticles. Using e-beam lithography, it is straightforward to prepare a pair of metal electrodes separated by a gap of tens of nanometers. When we place these electrodes across the nanoparticle chain (Figure 1c), many of the inter-electrode gaps are bridged by just one nanoparticle.

In Figure 3a, we show the low temperature conductance of a SET made from a 50 nm nanoparticle. Many single-electron conductance oscillations are visible as a function of gate voltage (applied to the conductive substrate). These data show very good reproducibility of the peak positions when the gate voltage is swept in opposite directions (-10 V to +10 V and back to -10 V). Particularly noticeable is the lack of any “offset charge” effects, which create discontinuous shifts of the conductance curves at random values of gate voltage. Offset charges are detrimental to the reliable operation of the

Coulomb blockade samples. Their absence indicates that the sample surface is relatively free of contaminants which can be randomly charged or discharged. APTES treatment makes the SiO₂ surface hydrophobic; we surmise that its water repellent effect may help to reduce the offset charges.

Figure 3b shows the conductance map of the same sample, measured as a function of the gate voltage and the source-drain bias. Here, we sweep the source-drain bias while the gate voltage is slowly stepped. The existence of offset charges would result in discontinuous vertical lines in the conductance map; the observed smooth conductance map clearly indicates the lack thereof. From the sizes of the “Coulomb diamonds” in Figure 3b we estimate the nanoparticle-gate capacitance as 0.3 aF and the nanoparticle capacitances to the source and drain \sim 10-30 aF. These values are reasonable consistent with previously reported values for a similar structure [13].

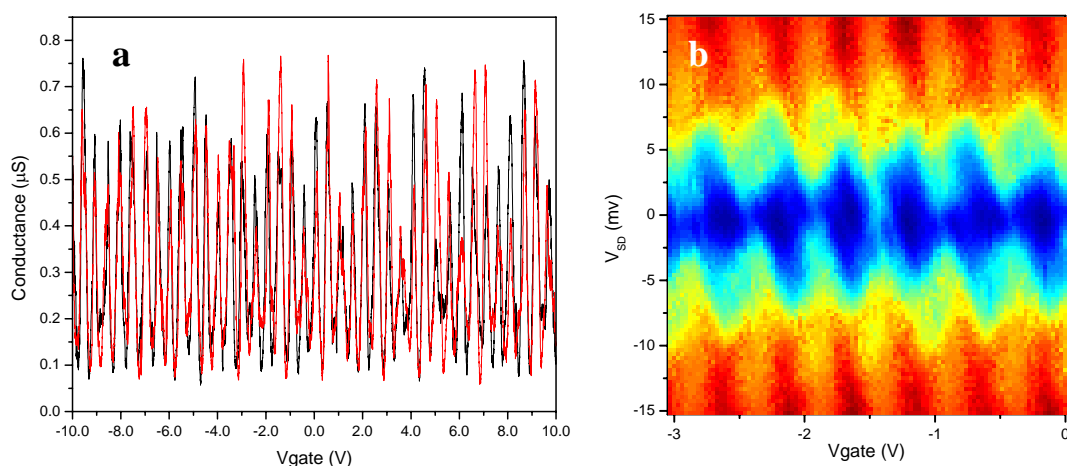



Figure 3. a) Coulomb blockade pattern in differential conductance $G=dI/dV$ measured as a function of gate voltage, V_{gate} , at 4.2 K. Note, that positions of the peaks coincide in the two superimposed traces, which were swept successively in opposite directions. This is an indication that “offset charges”, that rigidly shift the segments of the $G(V_{gate})$ curve, are absent. Also noticeable is the width of the peaks, greatly exceeding the possible temperature broadening. The width is explained by the lifetime broadening, which indicates low tunneling barriers and good coupling of the nanocrystal to at least one of the leads.

b) “Coulomb diamonds” in conductance measured as a function of the gate voltage and the source-drain bias. Note the smooth pattern, again lacking the rigid “offset charging” events. Colormap: 0  2.2 μ S.

Control of length and directionality of DNA superstructures

In our recent paper [14], we presented constructions consisting of heterogeneous DNA motifs using dsDNA in conjunction with complex, cross-tile building blocks. We demonstrated control of length and directionality of superstructures by incorporation of dsDNA bridges in stepwise assembly processes. This strategy is analogous to on-the-fly “reprogramming” of the sticky-ends displayed on DNA tiles.

Specifically, we demonstrated dsDNA nanobridges joining preformed lattice pieces in controlled ways. Two distinct self-assembled DNA superstructures were implemented and observed by atomic force microscopy: (i) finite-size lattice formed from

2 x 2 nanoarrays plus dsDNA bridges and (ii) extended lattices formed from nanotracks plus dsDNA bridges (Figure 4).

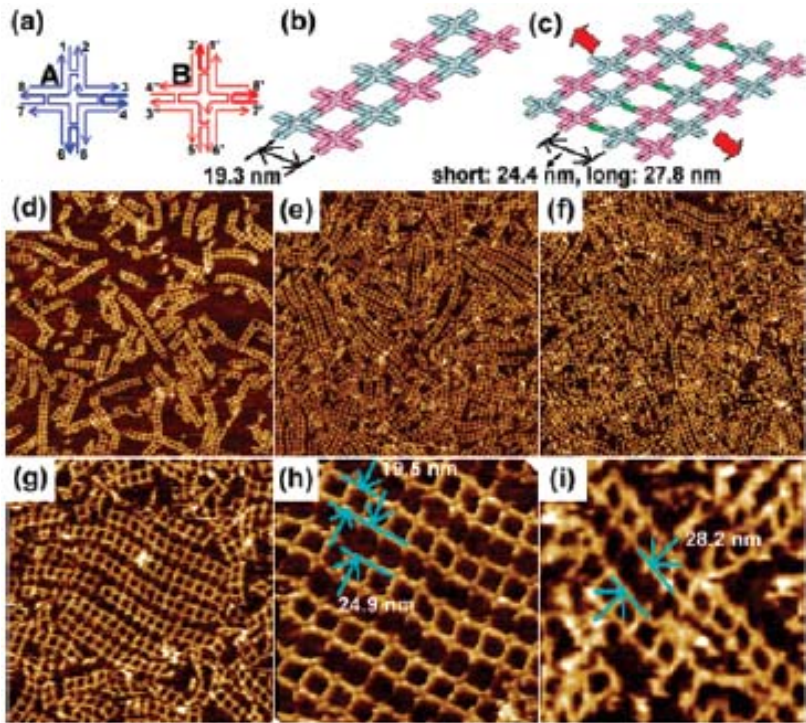


Figure 4. Schematics: (a) Drawings of A and B cross-tiles, (b) cartoon of a nanotrack (NT), (c) NT with dsDNA bridges. Red arrows indicate growth-directions due to the possibility of assembling additional dsDNA bridges. AFM images (1 x 1 μm scans): (d) NT without bridges, (e) NT with shortbridges, and (f) NT with long-bridges; (g and h) high-resolution AFM images of NTs with short-bridges (500 x 500 nm and 200 x 200 nm scans); (i) AFM image of NTs with long-bridges (200 x 200 nm scan). Observed dimensions are in good agreement with designed structures

Reconfigurable DNA-nanoparticle assemblies for plasmonics

Molecular control of plasmon coupling is investigated in sub-100 nm assemblies composed of 13 nm gold “satellite” particles tethered by reconfigurable DNA nanostructures to a 50 nm gold “core” particle. Reconfiguration of the DNA nanostructures from a compact to an extended state results in blue shifting of the assembly plasmon resonance, indicating reduced interparticle coupling and lengthening of the core-satellite tether. In a separate experiment, controlled plasmon coupling is observed in nanoparticle assemblies composed of 20 nm silver ‘satellite’ nanoparticles tethered by reconfigurable duplex DNA linkers to a 50 nm gold ‘core’ particle. The assemblies incorporate silver nanoparticle–oligonucleotide conjugates prepared using a new conjugation method in which the recognition strand is anchored by a 10 base pair, double strand spacer that presents adjacent 3’- and 5’-thiols to the silver surface. The structural basis for the observed resonance modulation is investigated through simulation of the scattering spectra of binary assemblies with various core–satellite separations. Additional simulations of core–satellite assemblies composed of gold satellite particles bound to silver cores and of assemblies composed entirely of silver particles are used to clarify the dependence of the coupling response on the composition of the components and their distribution within the assembly [15, 16].

REFERENCES

1. S.H. Park, M.W. Prior, T.H. LaBean and G. Finkelstein, *Optimized fabrication and electrical analysis of silver nanowires templated on DNA molecules*. Applied Physics Letters **89**, p. 033901 (2006).
2. E. Braun, Y. Eichen, U. Sivan and G. Ben-Yoseph, *DNA-templated assembly and electrode attachment of a conducting silver wire*. Nature **391**, p. 775-778 (1998).
3. J. Richter, R. Seidel, R. Kirsch, M. Mertig, W. Pompe, J. Plaschke and H.K. Schackert, *Nanoscale palladium metallization of DNA*. Advanced Materials **12**, p. 507-+ (2000).
4. W.E. Ford, O. Harnack, A. Yasuda and J.M. Wessels, *Platinated DNA as precursors to templated chains of metal nanoparticles*. Advanced Materials **13**, p. 1793-1797 (2001).
5. K. Keren, M. Krueger, R. Gilad, G. Ben-Yoseph, U. Sivan and E. Braun, *Sequence-specific molecular lithography on single DNA molecules*. Science **297**, p. 72-75 (2002).
6. F. Patolsky, Y. Weizmann, O. Lioubashevski and I. Willner, *Au-nanoparticle nanowires based on DNA and polylysine templates*. Angewandte Chemie-International Edition **41**, p. 2323-2327 (2002).
7. C.F. Monson and A.T. Woolley, *DNA-templated construction of copper nanowires*. Nano Letters **3**, p. 359-363 (2003).
8. T. Scheibel, R. Parthasarathy, G. Sawicki, X.M. Lin, H. Jaeger and S.L. Lindquist, *Conducting nanowires built by controlled self-assembly of amyloid fibers and selective metal deposition*. Proceedings of the National Academy of Sciences of the United States of America **100**, p. 4527-4532 (2003).
9. U.C. Coskun, H. Mebrahtu, P.B. Huang, J. Huang, D. Sebba, A. Biasco, A. Makarovski, A. Lazarides, T.H. LaBean and G. Finkelstein, *Single-electron transistors made by chemical patterning of silicon dioxide substrates and selective deposition of gold nanoparticles*. Applied Physics Letters **93**, p. 123101 (2008).
10. R.G. Freeman, K.C. Grabar, K.J. Allison, R.M. Bright, J.A. Davis, A.P. Guthrie, M.B. Hommer, M.A. Jackson, P.C. Smith, D.G. Walter and M.J. Natan, *Self-Assembled Metal Colloid Monolayers - An Approach To Sens Substrates*. Science **267**, p. 1629-1632 (1995).
11. A.N. Shipway, E. Katz and I. Willner, *Nanoparticle arrays on surfaces for electronic, optical, and sensor applications*. Chemphyschem **1**, p. 18-52 (2000).
12. K. Sarveswaran, W.C. Hu, P.W. Huber, G.H. Bernstein and M. Lieberman, *Deposition of DNA rafts on cationic SAMs on silicon [100]*. Langmuir **22**, p. 11279-11283 (2006).
13. D.N. Weiss, X. Brokmann, L.E. Calvet, M.A. Kastner and M.G. Bawendi, *Multi-island single-electron devices from self-assembled colloidal nanocrystal chains*. Applied Physics Letters **88**, p. (2006).
14. S.H. Park, G. Finkelstein and T.H. LaBean, *Stepwise self-assembly of DNA tile lattices using dsDNA bridges*. Journal Of The American Chemical Society **130**, p. 40-+ (2008).
15. D.S. Sebba, T.H. LaBean and A.A. Lazarides, *Plasmon coupling in binary metal core-satellite assemblies*. Applied Physics B-Lasers And Optics **93**, p. 69-78 (2008).
16. D.S. Sebba, J.J. Mock, D.R. Smith, T.H. LaBean and A.A. Lazarides, *Reconfigurable core-satellite nanoassemblies as molecularly-driven plasmonic switches*. Nano Letters **8**, p. 1803-1808 (2008).