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DNA-templated Assembly of Nanowires and Protein-functionalized Nanocontacts

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We describe the use of DNA to template the assembly of gold nanowires between conventionally patterned gold contacts on a silicon wafer substrate. We also describe the use of DNA to template the assembly of protein-functionalized gold nanocontacts on a silicon wafer substrate. Of particular significance is the finding that suitably modified gold nanoparticles recognize and bind selectively the protein-functionalized nanogap between the above contacts and are localized there.

Keywords: DNA; Protein; Template; Nanowires; Nanocontacts

INTRODUCTION

The demand for integrated circuits that will allow information be processed at ever faster speeds remains undiminished. This is despite the fact that, as a result of miniaturization, the density of the wires and switches that comprise such circuits has doubled every 18 months, giving rise to Moore's law [1]. While it is expected that Moore's law will hold true until 2012, it is not currently expected that it will hold true thereafter for two reasons [2]. The first reason is that to build smaller wires and switches requires major advances in established fabrication and materials technologies. Specifically, it requires the development at great cost of new light sources and process tools, new mask and resist materials, and new high and low dielectric constant materials. The second reason is that as wires and switches become smaller, the materials of which they are composed no longer exhibit bulk properties, but exhibit properties dominated by confinement and surface effects.

The responses of the related scientific and engineering communities have been twofold. The first has been to develop alternative fabrication technologies, and the second has been to propose new integrated circuit architectures that can accommodate or even exploit the novel properties exhibited by these smaller wires and switches.

When contemplating alternative fabrication technologies, one is immediately attracted to the self-assembly in solution and self-organization at a conventionally patterned silicon wafer substrate of nanoscale wires and switches [3]. When contemplating alternative materials technologies, one is immediately attracted to the use of biological molecules as templates and modified nanoparticles as building blocks [4,5]. It is noted that there have been a number of recent reports that have demonstrated the potential of these and related approaches [6–10].

It is in this context that we describe the use of DNA to template the assembly of nanowires and protein-functionalized nanocontacts in solution. Specifically, we describe the use of DNA to template the assembly of gold nanowires between conventionally patterned gold contacts on a silicon wafer substrate [11]. We also describe the use of DNA to template the assembly of protein-functionalized gold nanocontacts on a silicon wafer substrate [12]. Of particular significance is the finding that suitably modified gold nanoparticles recognize and bind selectively the protein-functionalized nanogap between the above contacts and are localized there.

RESULTS AND DISCUSSION

DNA-templated Assembly of Gold Nanowires

The strategy adopted is illustrated in Scheme 1 and comprises the following steps. First, double-stranded

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calf-thymus DNA is deposited between conventionally patterned gold contacts on a silicon wafer substrate. Second, the above wafer is exposed to an aqueous dispersion of positively charged 4-dimethylaminopyridine (DMAP)-stabilized gold nanoparticles, which are selectively adsorbed at the negatively charged DNA template. Third, the adsorbed nanoparticles are enlarged and enjoined by electrodeless deposition to form a continuous nanowire. Having templated the assembly of the above nanowire, it is characterized electronically.

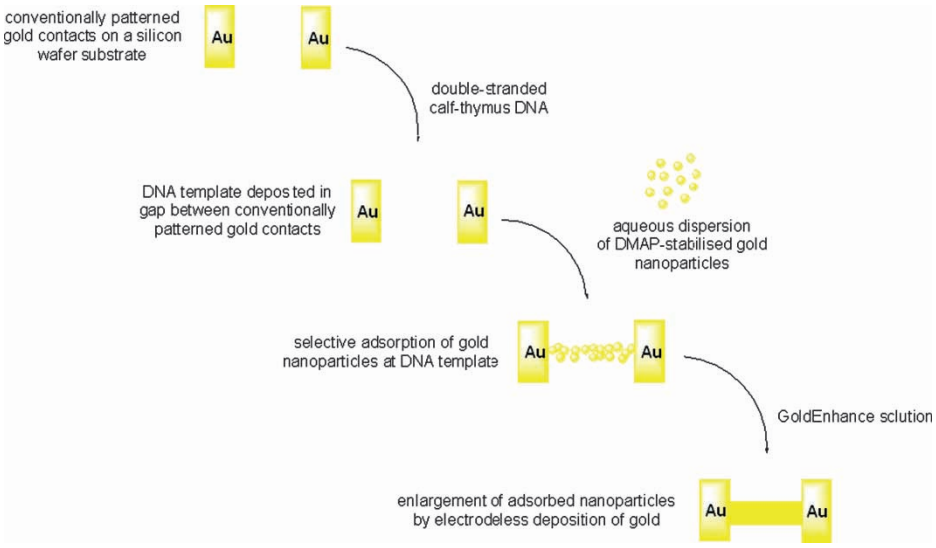
Specifically, a drop of the calf-thymus DNA template solution was deposited on a plasma-treated silicon wafer substrate patterned with interdigitated gold contacts (1 μm spacing). Subsequent spin coating elongated the DNA template. Plasma treatment improved the binding of the DNA template to the oxide layer. Following elongation and immobilization of the DNA template on the above substrate, a drop of DMAP-stabilized gold nanoparticle dispersion was deposited on the silicon wafer substrate. It has been established, by Zeta potential measurements, that these particles are positively charged. As a consequence, they are selectively adsorbed at the negatively charged DNA-backbone of the template. Nanoparticle adsorption was immediate, so that an exposure time of 1 min sufficed. It should be noted, however, that the DMAP-stabilized gold nanoparticles adsorbed at the partially metallized DNA template do not form a continuous wire. This is not an unexpected finding in light of the fact that positively charged gold nanoparticles repel each other.

Accordingly, the partially metallized calf-thymus DNA template was exposed to a solution that caused the adsorbed gold nanoparticles to be enlarged and enjoined and to form a continuous polycrystalline nanowire. Specifically, the partially metallized DNA template on a silicon wafer substrate was exposed to a GoldEnhance® solution. Under these conditions, gold nanoparticles adsorbed at the partially metallized DNA template act as sites for the catalytic deposition of gold and are enlarged. As a result, these gold nanoparticles are enjoined and form a continuous polycrystalline gold nanowire. The diameter of the nanowire formed depends on the exposure time.

Shown in Fig. 1 is an SEM of one such electrode after all of the above steps had been completed. These images confirm the templated assembly of a network of polycrystalline gold nanowires across the 1.0 μm gap between electrodes. It should be noted that these wires have been assembled on top of the previously deposited gold electrodes.

Two-terminal current-voltage measurements were made for the network of nanowires shown in Fig. 3 and yielded the linear ohmic relationship shown in Fig. 2. The measured total resistance was 103 kΩ.

The dimensions of the nanowires in Fig. 1 were obtained from an analysis of the above SEM (40 nm width and 1.25 μm length) and the corresponding AFM (20 nm height). This yields a cross-sectional area of $8 \times 10^{-16}\,m^2$. The number of nanowires contributing to charge transport (between 1 and 6) was obtained from an analysis of the same SEM image. The value estimated for three interconnecting wires was taken as representative. This yielded a single wire resistivity of $2 \times 10^{-4}\,\Omega m$, a value four orders of magnitude larger than the resistivity of bulk polycrystalline gold ($2 \times 10^{-8}\,\Omega m$) [11]. We compare this finding with those reported by others for DNA-templated polycrystalline gold nanowires.



SCHEME 1 Strategy for DNA-templated assembly of gold nanowires.

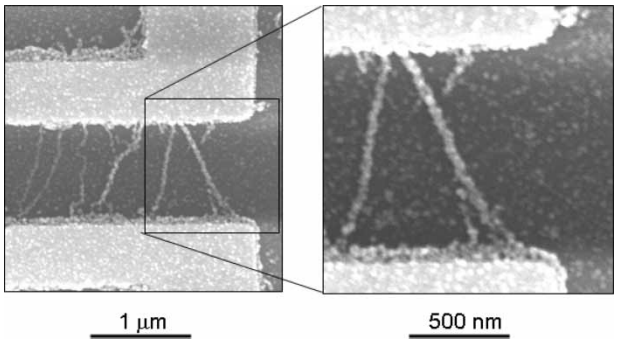


FIGURE 1 SEM image of a network of gold nanowires self-assembled between parallel 1 μm gold electrodes.

Until recently the lowest resistivity was that reported by Keren *et al.* [8]. These workers reported a value of $2 \times 10^{-7}\,\Omega$m. This value was obtained for an aldehyde-modified DNA template deposited on a passivated silicon wafer substrate. The aldehyde groups on the DNA template reduced silver ions from solution, leading to the formation of silver clusters. These silver clusters seeded the subsequent electrodeless deposition of gold on the DNA template and the formation of a continuous polycrystalline wire. Gold electrodes were overlaid on the above nanowire to permit electrical characterization. The next lowest values were those reported by Harnark and colleagues [13–15]. These workers reported a resistivity of $3 \times 10^{-5}\,\Omega$m [14]. This value was obtained for a DNA template deposited on a plasma-treated silicon wafer substrate on which gold electrodes had previously been deposited. The DNA template was exposed to a dispersion of tris(hydroxymethyl) phosphine (THP)-modified gold nanoparticles (about 2 nm diameter), which bind strongly to the DNA template. Subsequent electrodeless deposition of gold resulted in these nanoparticles being enlarged and enjoined and led to the formation of a network of continuous polycrystalline nanowires. Their stated resistivity was calculated by cutting one of the above wires and observing the change in the measured resistance. A change in the measured resistance of 2.4 kΩ resulted from cutting a nanowire that was 126 nm in diameter. Harnack *et al.*, have recently repeated this experiment for a 130 nm diameter wire on which gold electrodes have been overlaid [15]. The calculated resistivity of $2 \times 10^{-7}\,\Omega$m is two orders of magnitude smaller than the value calculated above for the same wire overlaid on gold electrodes.

Clearly, there is a large contribution to the resistivity calculated for our calf-thymus DNA-templated polycrystalline gold nanowires from the contact resistance. This contribution can be significantly reduced by overlaying the electrodes on the templated nanowires. This work is currently in progress. Equally clearly, there are contributions to the resistivity calculated for our and others' DNA-templated polycrystalline gold nanowires from grain boundary and surface scattering resistances [16]. A further contribution from constrictions along the length of the wire is likely to be significant [17]. Currently, we are measuring the temperature-dependent resistance of a series of DNA-templated polycrystalline gold nanowires overlaid on electrodes and on which electrodes have been overlaid. These nanowires have been prepared using particles of different diameters that have been enlarged to different extents and in some cases thermally annealed. By this means, the relative magnitudes of the above contributions to the calculated resistivities can be elucidated.

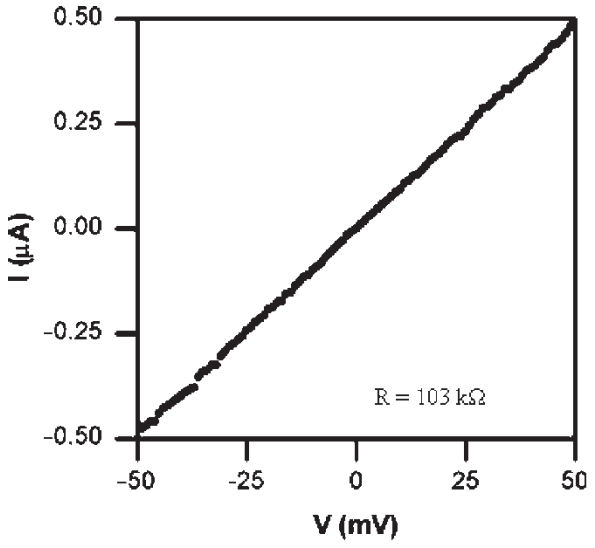
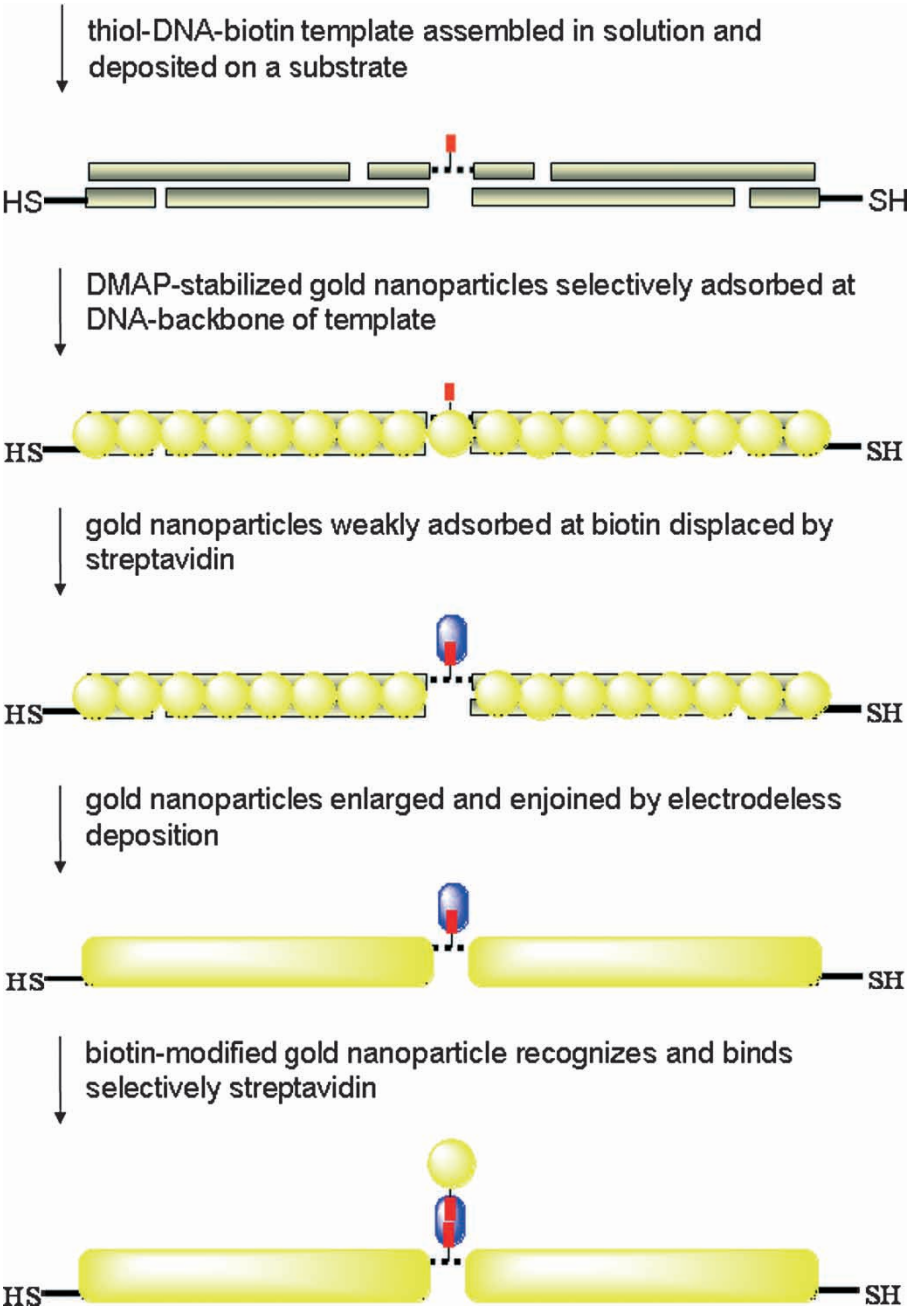


FIGURE 2 Plot of current *vs.* voltage at room temperature of the network of gold nanowires in Fig. 1. These nanowires exhibit linear ohmic behaviour and an overall resistance of 103 kΩ.

DNA-templated Assembly of Protein-functionalized Gold Nanocontacts

The strategy adopted is illustrated in Scheme 2 and is composed of the following steps. First, a thiol–DNA–biotin template is deposited on a silicon wafer substrate. In future it is intended that the thiol groups will locate the template in the gap between the conventionally patterned gold contacts. Second, the substrate is exposed to a dispersion of DMAP-stabilized gold nanoparticles. These nanoparticles are adsorbed selectively at the DNA backbone of the template, leading to its partial metallization. Third, the substrate is exposed to a dispersion of the protein streptavidin. A streptavidin recognizes and binds selectively the biotin located at the midpoint of the template. Moreover, any partially bound gold nanoparticles in the vicinity of the biotin are displaced, resulting in the creation of a streptavidin-functionalized gap. Fourth, electrodeless deposition is used to enlarge and enjoin the gold

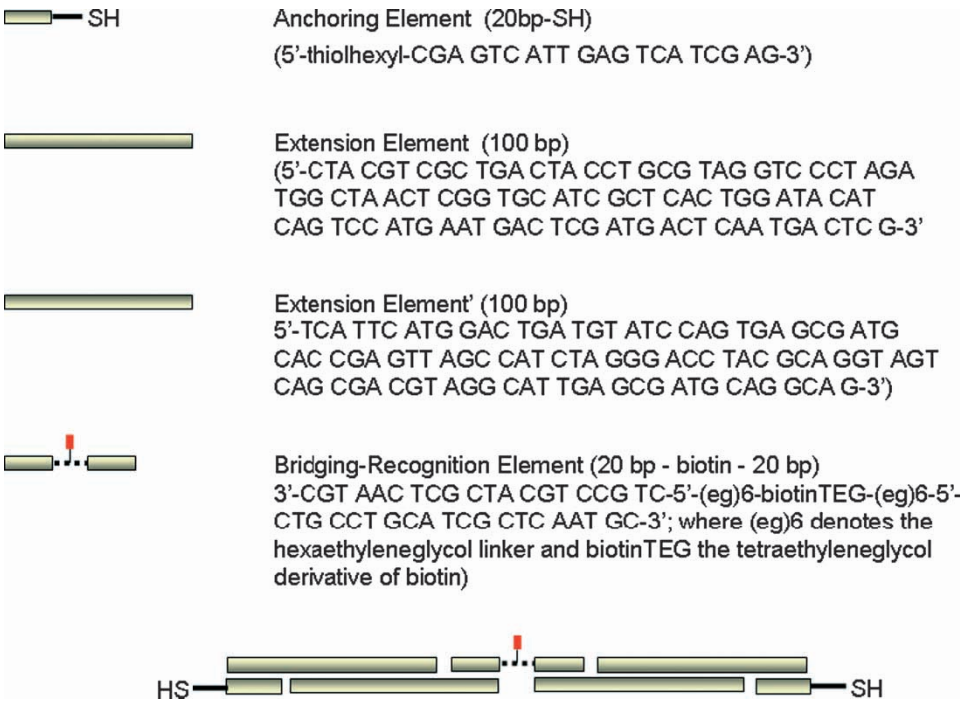


SCHEME 2 Strategy for DNA-templated assembly of gold nanocontacts with a protein-functionalized nanogap.

nanoparticles adsorbed at the DNA-backbone of the template. This leads to the complete metallization of the DNA-backbone. Finally, the streptavidin-functionalized nanogaps between the above contacts are exposed to a dispersion of biotin-modified gold nanoparticles. These nanoparticles recognize and bind selectively the streptavidin and are localized in the gap.

Specifically, the thiol–DNA–biotin template shown in Scheme 3 consists of the following elements: two *anchoring elements*, each a thiol-terminated 20-base oligomer; four *extension elements*, two pairs of complementary 100-base oligomers; and one *bridging-recognition element*, two 20-base oligomers linked by a hexaethyleneglycol moiety incorporating at the midpoint a biotin. This template was assembled in solution by hybridizing the above elements.

Once assembled, the template was purified and deposited on an unpatterned silicon wafer substrate. An AFM of the template (Fig. 3a) shows it to be 90 nm long and approximately 1 nm high. These findings are consistent with the expected structure of the template (Fig. 2) and also with recently reported findings for the assembly and structural characterization of a closely related model template [18].



SCHEME 3 Thiol–DNA–biotin template for assembly of gold nanocontacts with a protein-functionalized nanogap.

The thiol–DNA–biotin template, deposited on a silicon wafer substrate, was exposed to dispersion DMAP-stabilized gold nanoparticles. It has been established, by Zeta potential measurements, that these particles are positively charged. As a consequence, they are selectively adsorbed at the negatively charged DNA-backbone of the template. An AFM of the template (Fig. 3b) shows that metallization has taken place. A TEM of a similar sample (Fig. 3c), on a carbon-coated TEM grid,

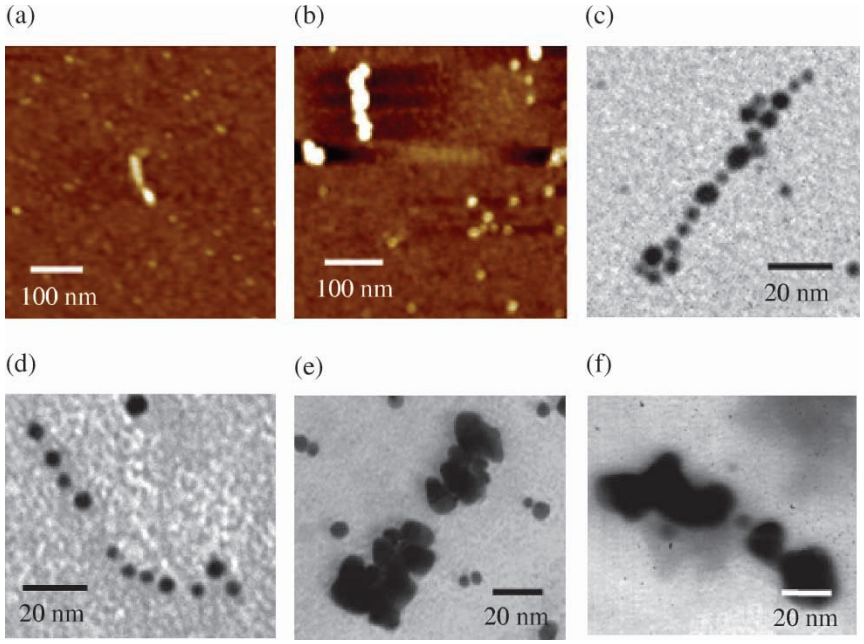


FIGURE 3 (a) AFM of a thiol–DNA–biotin template on a silicon wafer substrate. (b) AFM of a partially metallized thiol–DNA–biotin template, again on a silicon wafer substrate. (c) TEM of a partially metallized thiol–DNA–biotin template on a carbon-coated copper grid. (d) TEM of a partially metallized thiol–DNA–biotin template on a carbon-coated copper grid, which has been exposed to streptavidin that binds the biotin moiety located at the midpoint of the template and displaces the gold nanoparticles located there. (e) TEM of a streptavidin-functionalized thiol–DNA–biotin template, which has been metallized by exposure to a GoldEnhance® solution and causes the gold nanoparticles to be enlarged and enjoined. (f) TEM of the metallized and streptavidin-functionalized template exposed to a dispersion of biotin-modified gold nanoparticles, which shows that these particles are localized in the gap.

shows that metallization is partial and extends over the entire length of the template. That this is the case is not unexpected as the adsorbed nanoparticles are all positively charged and repel each other.

The partially metallized thiol–DNA–biotin template was exposed to a dispersion of the tetrameric protein streptavidin, which is known to have a very high affinity for biotin [19]. As was expected, and as may be seen from the corresponding TEM (Fig. 3d), the streptavidin recognizes and binds selectively the biotin located at the midpoint of the template and displaces the weakly bound DMAP-stabilized gold nanoparticles. The size of the gap formed, approximately 15 nm, is consistent with the dimensions of the essentially box-like tetrameric protein ($5 \times 4 \times 4$ nm). It should be noted that subsequent exposure of this sample to a dispersion of biotin-modified gold nanoparticles (16 nm diameter) resulted in the gold nanoparticles recognizing and binding selectively the streptavidin located in the gap (Fig. 4a). It should also be noted that previous exposure to a biotin solution prevented these nanoparticles being adsorbed in the gap (Fig. 4b). Finally, unmodified nanoparticles (16 nm diameter) were not adsorbed in the gap (Fig. 4c). On this basis it can be concluded that the gap is streptavidin functionalized.

The partially metallized and streptavidin-functionalized thiol–DNA–biotin template was exposed to a GoldEnhance® solution. As was expected, and as may be seen from the corresponding TEM (Fig. 3e), the template was completely metallized by catalytic deposition of gold on the existing adsorbed gold nanoparticle, which caused these nanoparticles to be enlarged and enjoined. This step also reduces the size of the gap to less than 10 nm but, as is discussed below, did not reduce the activity of the streptavidin localized in the gap.

The metallized and streptavidin-functionalized 10 nm gap between the nanocontacts was exposed to a dispersion of biotin-modified gold nanoparticles (5 nm diameter). As was expected, and as may be seen to be the case (Fig. 3f), a biotin-modified gold nanoparticle recognizes and binds selectively the streptavidin localized in the 10 nm gap. The overall yield of the templated assembly shown in Fig. 3f is estimated to be 60%.

It should be noted that, in a related control experiment, it was found that deactivating the streptavidin by exposure to a solution of biotin molecules (Fig. 4d) did not lead to localization of gold nanoparticles in the 10 nm gap. On this basis it is concluded that adsorption of the biotin-modified gold nanoparticle in the streptavidin-functionalized 10 nm gap between the nanocontacts is a recognition-driven and selective process.

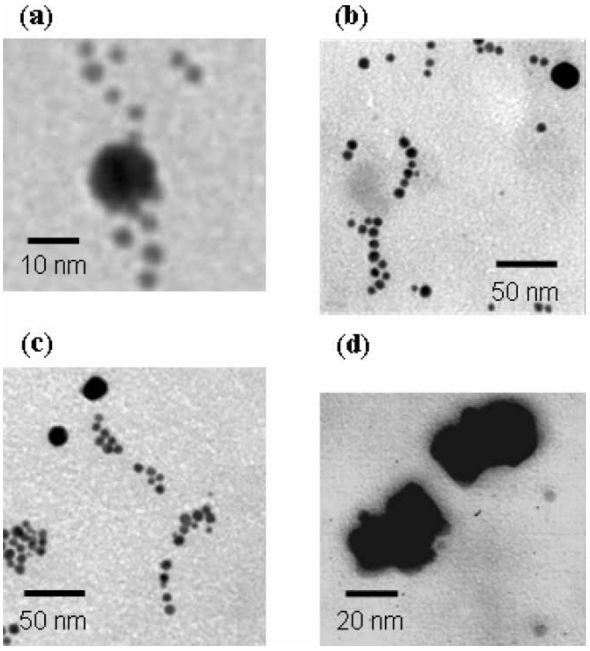


FIGURE 4 TEMs of control experiments in which the sample: (a) in Fig. 3d was exposed to a dispersion of 16-nm diameter biotin-modified gold nanoparticles; (b) in Fig. 3d was initially exposed to a biotin solution and was subsequently exposed to a dispersion of 16-nm diameter biotin-modified gold nanoparticles; (c) in Fig. 3d was exposed to a dispersion of 16-nm diameter unmodified gold nanoparticles; and (d) in Fig. 3f was initially exposed to a biotin solution and was subsequently exposed to a dispersion of 5-nm diameter biotin-modified gold nanoparticles.

CONCLUSIONS

The findings presented here demonstrate that it is possible to use biological molecules, specifically DNA, to template the assembly of nanoparticles, specifically gold nanoparticles, in solution and at patterned substrates. These and related findings represent progress towards the development of a scalable bottom-up fabrication technology for the assembly and organization of integrated arrays of nanoscale wires and switches.

EXPERIMENTAL

General experimental details have been reported in a series of related papers [18,20]. Specifically, we have reported the synthesis and characterization of the modified DNA oligomers used to assemble the templates themselves [20]. We have also reported the assembly and characterization of the above DNA templates and their subsequent use in the assembly of model nanoparticle architectures in solution [18].

Specific experimental details have been reported in two papers describing the calf-thymus DNA templated assembly of gold nanowires [11] and protein-functionalized gold nanogap contacts [12].

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