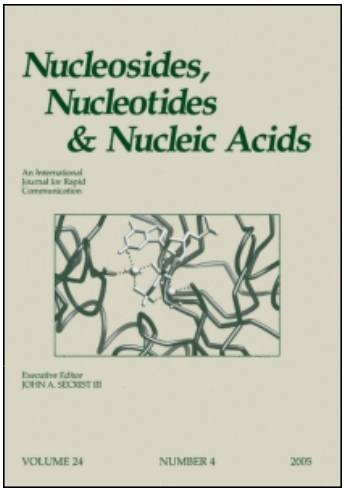

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A FLEXIBLE METHOD FOR THE FABRICATION OF GOLD NANOSTRUCTURES USING OLIGONUCLEOTIDE DERIVATIVES

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□ *Several linear and branched DNA structures from 80–200 nm with a biotine molecule in the middle have been prepared. These structures have been decorated by addition of positively charged gold nanoparticles carrying 4-(dimethylamino)pyridine ligands. Streptavidin binds to the central biotine molecule introducing a 20 nm gap in the structure in which a biotinylated nanoparticle can be introduced. The simplest structure (80 nm, linear) is formed by 4 oligonucleotides. By changing some of these components changes on length, shape, and recognition system easily can be introduced.*

Keywords Gold nanoparticles; self-assembly; DNA nanobiotechnology

INTRODUCTION

Among the biological molecules, oligonucleotides have been used as template to assemble inorganic nanocrystals, especially gold nanoparticles.[1,2] The hybridization properties of the oligonucleotides allow the assembly of gold nanoparticles at distances determined by the length of the oligonucleotides and also the formation of three-dimensional networks.[1,2] Also, oligonucleotides linked to nanoparticles have special optical properties used for monitoring DNA hybridization.[3] In addition DNA can be metalized to form conducting wires between electrodes.[4] In the present communication we will describe the use of oligonucleotides to obtain functional units with potential interest in nanoelectronics.

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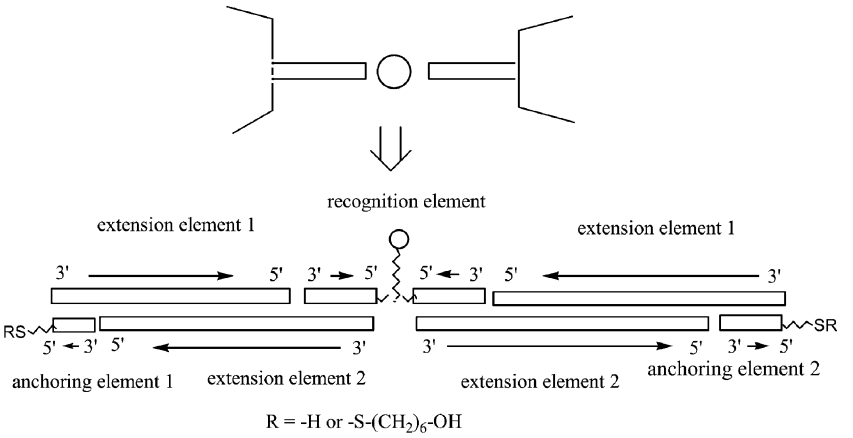

SCHEME 1 Outline of target nanoscale assembly.

RESULTS AND DISCUSSION

We are interested in the preparation of synthetic DNA derivatives designed to assemble a molecular wire between two or three gold electrodes, which are needed to address individual nanoparticles from macroscopic electrodes.[5–8] Synthetic oligonucleotides were used to prepare the molecular wires, offering the possibility to introduce modifications at any predetermined position.

The simplest target molecule consists of three elements having different roles: anchoring, extension, and recognition (Scheme 1). Two anchoring elements are located at each end, both having disulfide groups allowing the wires to be attached to the electrodes. The center of the structure is a chimeric compound with a DNA segment that positions the element in the middle of the structure. It also contains biotin as a recognition group, isolated from the DNA by a spacer molecule made of two hexaethylenglycol units. This recognition element is used to direct a nanoparticle into the middle of the structure as well as to connect the two branches. The size of the whole structure is determined by the extension elements between the recognition and the anchoring elements.

Figure 1 shows the AFM image (tapping mode) of a target assembly connected to two gold nanoparticles of 5 nm. Significantly, both the gold nanoparticles and DNA backbone components can be seen. The center-to-center distance between the nanoparticles (73 nm) is close to the expected value of the assembly (80 nm). Figure 2 shows the AFM image of a longer assembly connected between two gold nanoparticles. In this case, eight oligonucleotides of 100 bases were used as extension elements instead of two obtaining a linear assembly of 280 nm.

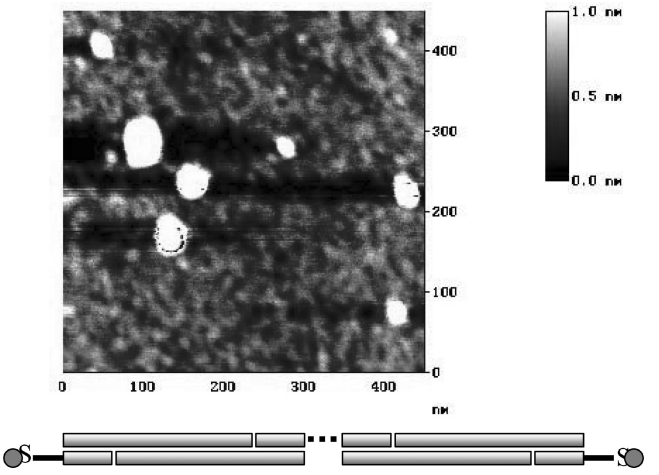

FIGURE 1 AFM image (tapping mode) of the nanoscale assembly shown in Scheme 1 (240 bp, nominal size 80 nm) connected to two gold nanoparticles of 5 nm.

Using these oligonucleotides the DNA-templated assembly of a protein-functionalized 10 nm gap electrode on a silicon wafer substrate, is being undertaken.[6–8] First the DNA lineal structures shown above are decorated by addition of 4-(dimethylamino) pyridine (DMAP) gold nanoparticles.[6,7] Second, streptavidin binds to the central biotine molecule introducing a 20 nm gap in the structure. Third, the DMAP-gold nanoparticles are increased in size by electrodeless deposition. Finally, the streptoavidin

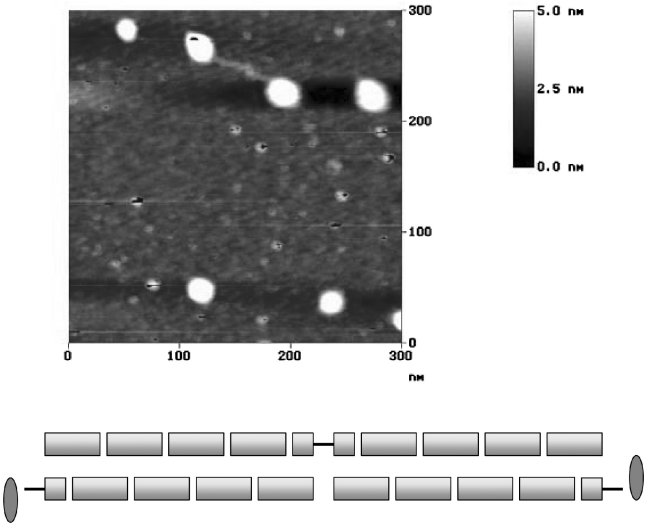

FIGURE 2 AFM image (tapping mode) of a long DNA assembly prepared using 8 extension elements of 100 bases (840 bp, nominal size 280) connected to two gold nanoparticles of 5 nm.

molecule in the center still is able to capture a single gold nanoparticle functionalized with biotine in the 10 nm gap.[6–8] These findings are of interest for the fabrication of next-generation electronic devices.

EXPERIMENTAL PART

Synthesis of Oligonucleotides

The general strategy is based on the solid-phase methodology using 2-cyanoethyl phosphoramidites as monomers. The syntheses were performed on an Applied Biosystems Model 3400 DNA synthesizer using 0.2 and 1 μmol scales. The extension elements (100 bases long) were prepared on 0.2 μmol scale using highly cross-linked polystyrene as solid support (LV200 columns, Applied Biosystems). Ammonia deprotection was performed overnight at 55°C. Oligonucleotides were prepared with the last DMT group at the 5′ end (DMT on protocol) to help reverse-phase purification. All purified products presented a major peak which was collected. HPLC solutions are as follows. Solvent A: 5% ACN in 100 mM triethylammonium acetate (pH 6.5) and solvent B: 70% ACN in 100 mM triethylammonium acetate pH 6.5. Columns: PRP-1 (Hamilton), 250 × 10 mm. Flow rate: 3 ml/minute. A 30 minutes linear gradient from 10–80% B (DMT on), or a 30 minutes linear gradient from 0–50% B (DMT off) were used.

Thiolated oligonucleotides were prepared on 1 micromol scale using standard phosphoramidites. For the introduction of the thiol group the phosphoramidite of hydroxyhexyldisulfide protected with the dimethoxytrityl group (thiol modifier C6 S-S, Glen Research) was used. Oligonucleotide carrying the thiol group was deprotected with concentrated ammonia containing 0.05 M DTT (16 hours, 55°C) and desalted with Sephadex G-25 (NAP-10) prior use. If concentrated ammonia without DTT is used, oligonucleotides with disulfide groups were obtained.

Special protocols were developed for the preparation of the recognition elements since the polarity of the DNA strands is reversed in the middle of the molecule, thereby providing symmetry to the central assembly. The two-armed recognition element was prepared by sequentially adding 10 different phosphoramidites. Starting from the 3′-end, the first half of the sequence was assembled using the four standard phosphoramidites. Subsequently, hexaethyleneglycol and biotin-tetraethyleneglycol phosphoramidites were added. Finally, the second half of the molecule was assembled using the four reversed phosphoramidites.[9] Synthesis of the oligonucleotides carrying three branches was conducted in similar fashion although a symmetric branching molecule was added. First, the 20 mer sequence was built in the 3′->5′ direction using standard phosphoramidites and the hexaethyleneglycol phosphoramidite. Then, the biotin-tetraethyleneglycol was added. Afterwards, a symmetric branching

phosphoramidite was added to the sequence. Finally, the rest of the desired sequence was assembled in the 5′->3′ direction using reversed phosphoramidites and the hexaethyleneglycol phosphoramidite.[9] Oligonucleotides were prepared with the last DMT group at the 5′ end (DMT on protocol) to help reverse-phase purification as described for the synthesis of long oligonucleotides.

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