# Electrical Conduction of Thiol Modified 60bp Poly(dG)-Poly(dC) DNA Molecules through Au Nanoparticles

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A novel transport measurement scheme of 60 base pairs of poly(dG)-poly(dC) DNA molecules using Au nanoparticles is devised and implemented. Thiol (-SH) terminations are synthesized at both 5' and 3' ends of the double stranded DNA molecules and they can be chemisorbed on the Au surface through sulfur atoms by covalent bonding. These thiol-modified ends make chemical bindings with Au nanoparticles and Au nano-gap electrodes, forming a stable electrode-DNA-nanoparticle-DNA-electrode conduction channel. This transport channel is self-formed and is stable due to robust bonding of thiol and Au. The current-voltage characteristic measured from our device shows a nonlinear behavior and the voltage gap is comparable to the result of previous experiment using the same molecules. This self-trapping method by thiol modified DNA molecules would also be a promising technique for efficient nanoparticle trapping.

**Key Words :** Au Nanoparticle, DNA Molecule, Self-trapping Method

## 1. Introduction

Dioxyriboneucleic Acid (DNA) is an important molecular material for the element of molecular electronics because of its unique advantages, such as nanometer-scale molecular wires, adjustable lengths, and self-assembly properties (Mirkin et al., 1996 ; Aviram and Ratner, 1974). Understanding electrical conduction mechanism through these DNA molecules is essential for biomolecular device applications, and furthermore, charge migration in DNA molecules is also related with the radiation damage and repair mechanism of DNA in biomechanical and biological implications (Dandliker et al., 1997 ; Chae and Lee, 2004 ; Lee et al., 2004). Recently, several experimental and theoretical research results have demonstrated electrical conducting behaviors of DNA molecules by direct electrical conductivity measurements (Okahata et al., 1998 ; Fink and Schonenberger, 1999 ; Porath et al., 2000 ; Kasumov et al., 2001 ; Yoo et al., 2001 ; Hwang et al., 2002 ; Li and Yan, 2001 ; Cuniberti et al., 2002). However, the exact charge transport mechanism is still unknown and controversies are on-going (Gómez-Navarro et al., 2000 ; Storm et al., 2001). One of the uncertainties in these conduction measurements is the formation of electrical contacts between DNA molecules and metal electrodes. It is not even easy to confirm, by using conventional microscopy techniques, whether nanometer-scale DNA molecules with the diameter of 2 nm and the length of several tens of nm are really in between metal

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electrodes.

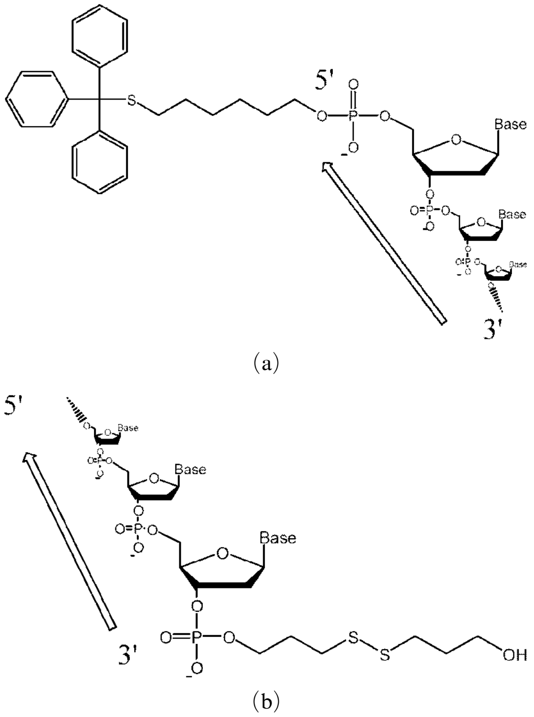
Thus, we introduce a novel method to clearly identify the DNA-electrode contacts and conduction through DNA molecules. Thiol (-SH) terminations, which can be chemisorbed on Au through sulfur, are attached at both ends of the DNA molecules. These thiol modified ends make chemical bonding with Au nanoparticles and Au nanoelectrodes, and form a stable electrode-DNA-nanoparticle-DNA-electrode conduction channel by a self-trapping process (Storm et al., 2001 ; Reichert et al., 2002 ; Hwang et al., 2004). In this paper, we report the electrical conduction measurement of our electrode-DNA-nanoparticle-DNA-electrode structure. This measurement demonstrates that poly(dG)-poly(dC) DNA molecules show a nonlinear transport behavior.

## 2. Experimental Procedure

Thiol modified 60 base pairs of poly (dG)-poly (dC) double stranded DNA molecules were prepared by synthesis of single stranded DNA molecules, thiol modification, and subsequent annealing process (Thiol-modified poly (dG) and poly (dC) DNA molecules were purchased from COSMO Co. Ltd.). The thiol modification was done at both 5’ and 3’ ends of the single stranded, 60 base pairs of poly(dG) and poly (dC) oligonucleotides. Fig. 1(a) and (b) show the chemical binding structures between DNA and thiol at 5’ and 3’ ends of the DNA molecules, respectively. Then both single stranded poly (dG) and poly (dC) oligonucleotides were annealed to form double stranded 60 base pairs poly(dG)-poly(dC) DNA molecules.

The thiol termination automatically remains in the double stranded DNA molecule after annealing. All the synthesis procedures were done in de-ionized water at the temperature of 97℃ and the concentration of the DNA solution was 1.25 $\mu$m. A protecting group is attached to sulfur to prevent chemical reaction between DNA molecules.

In order for the thiol-modified oligonucleotides to be reactive, they are treated with the mixed solution of TEAA (triethylammonium



(a)

(b)

**Fig. 1** Chemical structures of thiol and binding structures between DNA and thiol at (a) 5’ and (b) 3’ ends of the DNA molecules.

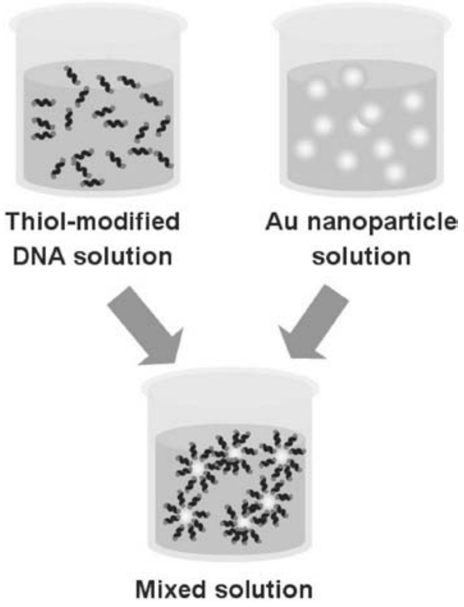


**Fig. 2** Schematic illustration of the formation of the Au nanoparticles with DNAs attached on their surfaces.

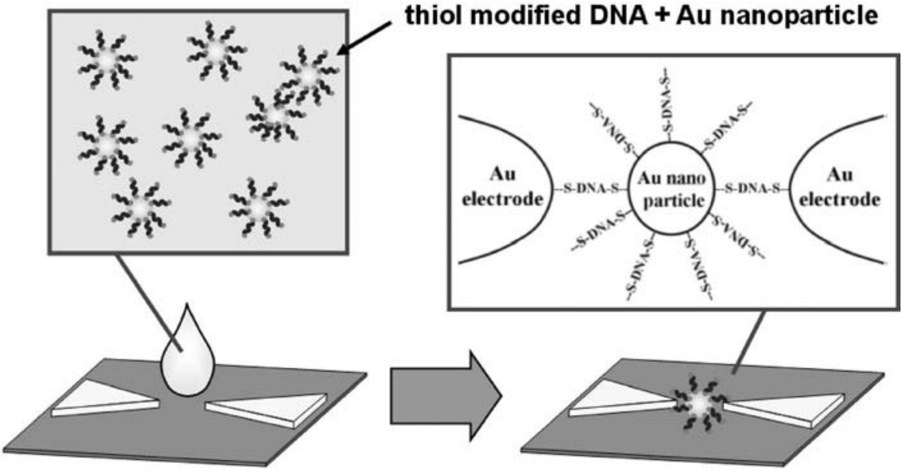


**Fig. 3** Conceptual diagram demonstrating the dropping process and the self-trapping of the Au nanoparticles with DNA molecules in between the Au nano-gap electrodes.

acetate) and DTT (dithiothreitol) for the 5' thiol, and DTT solution for the 3' thiol. Oligonucleotides treated with DTT solution are desalted on a gel filtration column to remove all the DTTs prior to synthesize. After removing of the protecting group, the DNA solution is mixed with a proper amount of Au nanoparticles. The DNA molecules were promptly attached to Au nanoparticles due to the thiol-Au bonding. The diameter and the concentration of the used Au nanoparticles are 20nm and 7×1011 particles/ml, respectively. Figure 2 schematically shows the formation of Au nanoparticles with the DNAs on their surfaces.

Nanometer-gap electrodes were fabricated by a standard electron-beam lithography and liftoff process on $SiO_2$/Si substrates. Thermal evaporation of a 5 nm Ti layer, followed by a 10 nm Au layer was used. Approximately 1 μl of the Au-DNA solution was dropped on the nano-gap electrodes with the separation of 50 nm. For about 10 s, self-trapping of nanoparticle between nano-gap electrodes occurred to form an electrical connection. The trapping was done by the bonding between the Au electrode and the free thiols of the DNA attached to Au nanoparticles.

Several hundreds of the thiol modified DNA molecules are chemically anchored their one ends to the surface of Au nanoparticles, and their other ends are ready to be anchored in the mixed solution. This makes possible that a DNA attached Au nanoparticle is easily self-trapped in between Au nano-gap electrodes when the mixed solution is dropped onto them. Residual droplets were dried with a flow of nitrogen gas. Figure 3 shows a conceptual diagram describing the trapping of the Au nanoparticle with thiol modified DNA molecules in between the Au nano-gap electrodes.

## 3. Results and Discussion

Figure 4 shows a scanning electron microscope (SEM) image of the nanoparticle with thiol modified DNA molecules in between nano-gap electrodes with the separation of 50 nm. It clearly shows that a single Au nanoparticle is trapped in between the nano-gap electrodes. Because the length of the DNA base pair is 0.34 nm, the length of the 60 base pairs DNA molecule in this study is approximately 20 nm. Therefore, the total length of the thiol modified DNA molecule is around 23 nm, taking into account the length of two thiol terminations at both ends. Considering slight bending of DNA molecules, we estimate the diameter of the DNA attached Au nanoparticle to be smaller than 66 nm which is the summation of twice the length of the thiol modified DNA molecules and the diameter of the Au nanoparticle. This size is viable for the self-trapping

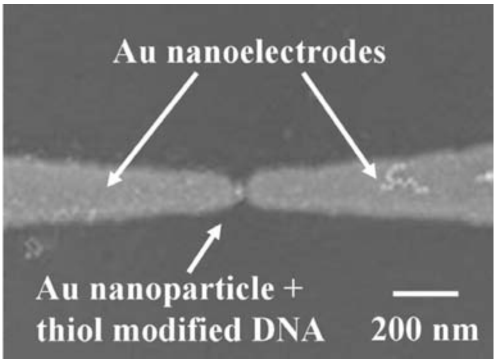


**Fig. 4** Scanning electron microscope image of Au nano-gap electrodes and the trapped Au nanoparticle with thiol modified DNA molecules. It clearly shows that a single Au nanoparticle with thiol modified DNA molecules is trapped in between Au nano-gap electrodes with the gap of 50 nm. By using this self-trapping method, we can obtain stable electrical conduction channel of Au electrode-DNA molecule-Au nanoparticle-DNA molecule-Au electrode configuration.

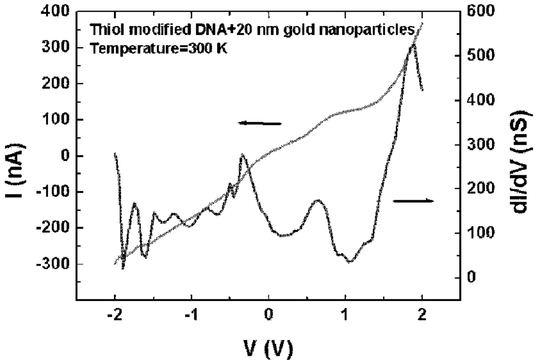


**Fig. 5** Room temperature I-V and dI/dV-V characteristics measured from the configuration of Fig. 4 at room temperature. The I-V curve shows nonlinear transport behavior with voltage gaps of 1.0 V and 1.3 V. The voltage gap is considered as the minimum energy to transfer electrons between DNA bases.

between the electrodes separated by 50 nm. Electrical connection in our method is expected to be more stable and reliable than other methods such as direct electrostatic trapping (Porath et al., 2000; Storm et al., 2001; Bezryadin et al., 1997). First of all, in the direct electrostatic trapping without Au nanoparticles, it is difficult to reliably fabricate electrode patterns with extremely small gaps. On the other hand, reliable fabrication of electrode patterns with the gap size comparable to the size of Au particle is much easier. Secondly, the identification of captured DNA molecules is almost impossible in the direct electrostatic trapping. However, in our case, identification of the Au particle between electrodes unambiguously guarantees the existence of DNA molecules in the conduction path.

After the self-trapping process, electrical conduction measurement was performed to determine the transport properties through the DNA molecules. Figure 5 shows the current-voltage (I-V) and the differential conductance-voltage (dI/dV-V) characteristics measured from the device of Fig. 4 at room temperature. The I-V curve shows nonlinear transport behavior with voltage gaps. Two voltage gaps of 1.0 V and 1.3 V are obtained from three observed maxima at -0.4 V, 0.6 V and 1.9 V in the dI/dV-V characteristics. These voltage gaps are consistent with the previously observed values from the same DNA molecules (Porath et al., 2000; Hwang et al., 2002). Theoretical calculation of nonlinear I-V behavior has been done (Li and Yan, 2001) and the results are consistent with out experiments. According to their model, the voltage gaps in the I-V characteristics suggest that the potential barrier exists between the base pairs of DNA molecules. We emphasize that direct trapping was used in the previous measurements and there was a statistical fluctuation.

Possible electrical transport mechanism in DNA molecules is suggested as hopping processes between DNA bases, and the voltage gap observed in Fig. 5 is considered as the minimum energy to transfer electrons between DNA bases (Porath et al., 2000; Hwang et al., 2002; Li and Yan, 2001). The contact between the Au electrodes and the thiol modified DNA molecules is stable and is a strong chemical binding. The Au-sulfur chemical contact has been reported as a stable contact in previous study (Reed et al., 1997). The mechanism of electron transport through the thiol-

Au contact is not fully understood at this point and we don't know how much contribution is made to the overall voltage gap from the thiol-Au contact. Further investigation is needed to provide a detailed explanation for the effect of the thiol termination. Another difficulty is that the shape of the electronic wavefunction in DNA molecules is very sensitive to the shape and condition of Au atoms attached to them (Weber et al., 2002; Yaliraki et al., 2002). Such variation could also result in the asymmetry in I-V characteristics. Finally, the I-V curves obtained from several scans during several days are all consistent with one another. It suggests the stability of our scheme.

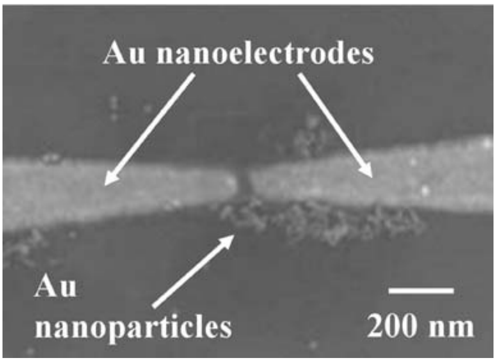


**Fig. 6** Scanning electron microscope image of Au nano-gap electrodes and trapped Au nanoparticles without thiol modified DNA molecules. A large number of Au nanoparticles are connected in between the Au nano-gap electrodes.

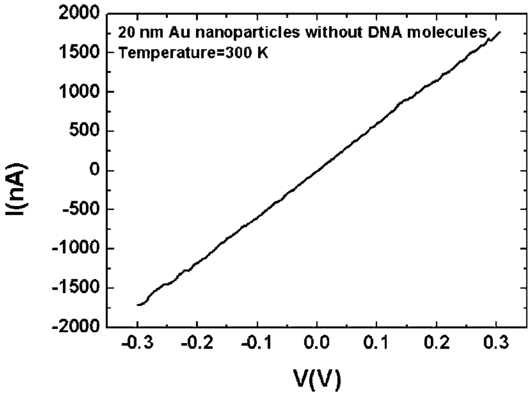


**Fig. 7** Room temperature I-V characteristic of Au nanoparticles without DNA molecules. Only linear behavior is observed and the average resistance is less than 1 MΩ.

In order to confirm our conducting behavior is really from DNA molecules, we trap a large number of Au nanoparticles without DNA molecules in between electrodes. Figure 6 is a SEM image of trapped Au nanoparticles in the electrodes. The I-V curve is also obtained from this sample and is shown in Fig. 7. Only linear behavior is observed from the electrical conduction measurement and the average resistance is less than 1 MΩ. The conductance value from the Au nanoparticles without DNA molecules is larger than that from the Au nanoparticle with DNA molecules. It suggest that the DNA molecules and thiols indeed participate in the transport in the data of Fig. 5.

## 4. Conclusion

In conclusion, we have demonstrated a novel method to clearly identify the electrical conduction behavior of DNA molecules. Thiol terminations are synthesized at both ends of the 60 base pairs of poly(dG)-poly(dC) DNA molecules and they are chemically anchored to the surface of Au nanoparticles. This thiol-modified DNA attached Au nanoparticle is self-trapped by the thiol terminations remained on the opposite side of the DNAs, in between Au nano-gap electrodes. This makes an electrical conduction channel of electrode-DNA molecule-nanoparticle-DNA molecule-electrode configuration.

The I-V curve measured from our structure shows a stable nonlinear transport behavior with voltage gaps, which suggests the minimum energy to transfer electrons between DNA bases. Only linear I-V behavior is observed from the electrical conduction measurement of Au nanoparticles without DNA molecules. Self-trapping method by thiol modified DNA molecules using Au nanoparticle can be applied to the bio-electromechancial systems and lab-on-a-chips. Observed electrical properties of DNA molecules could provide valuable information in the study of mechanical properties of DNA molecules.

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