Supplementary Material

Spin specific electron transport through DNA oligomers

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Sample preparation.

Nickel film- A 25 nm titanium (Kurt, 99.9%) adhesive layer was deposited at a rate of 0.1 nm/s on polished silicon p-type (100) wafer (0-100Ω/cm) followed by the deposition of 200 nm of Ni at 0.1-0.2 nm/s.[1] Ni (CERAC, 99.9995%). The deposition was carried out at a base pressure of 10^{-5} mbar in an electron beam evaporator. 1 cm^2 dies were cut out from the wafer for the following sample preparation.

Prior to electrochemical reduction of the oxide layer formed on the Ni, the Ni substrates were boiled in acetone and ethanol for 20 minutes each. The electrochemical reduction was carried out at -1.0 V with a saturated Calomel electrode (SCE reference electrode) for 20 minutes in 1M $HClO_4$ aqueous solution.[2] The set-up for the electrochemical process is shown in Figure S1. After the reduction, the Ni electrode was rinsed immediately in acetone and ethanol to remove the acid and to prevent formation of a new oxide layer. The Ni substrates were never dried or exposed to air prior to the adsorption of the DNA.

DNA adsorption on Nickel

3' thiol modified single strand DNA oligonucleotides (Integrated DNA technologies Inc.) were dissolved in ethanol at a concentration of 10 μM (90% ethanol V/V). 30 μl of this ssDNA solution was dropped on the Ni surface immediately after the oxide layer was removed. The adsorption of the ssDNA was carried out at room temperature in a controlled ethanol vapor pressure environment for 2 hours. After the adsorption, the

samples were rinsed thoroughly with ethanol and water, followed by a final rinse with the hybridization buffer just prior to hybridization. The ssDNA adsorption on electrochemical treated Ni surface was confirmed by radioactive labeling.

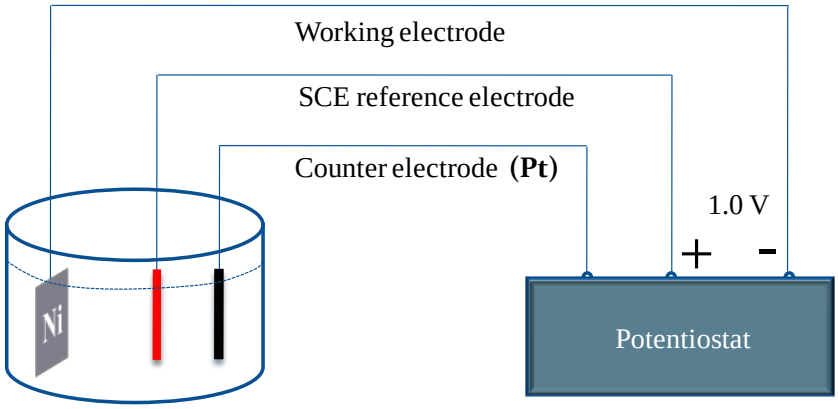

Figure S1: Electrochemical set up, for the reduction of the Ni oxide.

DNA adsorption on gold nanoparticles (GNPs).

The thiol- modified DNA oligonucleotides were kept in their oxidized form DNA-$(CH_2)_3$-S-S-$(CH_2)_3$-OH, in order to protect the thiol group from undesired oxidation products or dimerization. Prior to adsorption, the DNA was incubated with 10 mM of Tris (2-carboxyethyl) phosphine (TCEP) in 100 mM Tris-HCl, pH 7.5. The mixture was incubated at room temperature for 30 min to allow reduction of the disulfide bond. The solution was then passed through a separation column (BioSpin 6, BioRad) pre-equilibrated with Mili-Q water. The high molecular weight DNA molecules were collected from the effluent, while the small molecular weight species (TCEP and the reduction product HS-$(CH2)_3$-OH, that could interfere with the DNA binding to gold)

were captured on the spin columns. Two methods were used for the adsorption as described in references 3 and 4. Briefly, 100 μl of 20 μM reduced thiolated ssDNA in ethanol was mixed with 15 μl of ~10 nm diameter GNP (Sigma) ~6A_{520} units/ml solution from which the surfactant was removed. After stirring overnight at room temperature, the GNPs were rinsed and centrifuged at 10000 relative centrifugal force (rcf) for 20 minutes. 25 μl of the DNA-GNP solution was put onto the Ni coated with the complementary ssDNA monolayer and kept in a temperature and humidity controlled environment overnight. After adsorption, the samples were rinsed in the hybridization buffer then gently in Mili-Q and dried by Ar flow.

The DNA sequences used:

All sequences are thiol modified at the 3' by (3'– $(CH_2)_3$–SH).

<u>50 base pair DNA</u>

5'AAAGAGGAGTTGACAGTTGAGCTAATGCCGATTCTTGAGAAGGTAGAGTA3'(binds to Ni)

3'TTTCTCCTCAACTGTCAACTCGATTACGGCTAAGAACTCTTCCATCTCAT5'(binds to GNPs)

<u>40 base pair DNA</u>

5'TCTCAAGAATCGGCATTAGCTCAACTGTCAACTCCTCTTT3'(binds to Ni)

3'AGAGTTCTTAGCCGTAATCGAGTTGACAGTTGAGGAGAAA5'(binds to GNPs)

<u>26 base pair DNA</u>

5'CAAACAAACAAACAAAAAAAAAAAAA3'(binds to Ni)

3'GTTTGTTTGTTTGTTTTTTTTTTTT5'(binds to GNPs)

Sample characterization

The electrochemical reduction of the Ni surface was verified by immersing Ni –coated substrates in 1 mM 1-Dodecanethiol ($C_{12}H_{25}SH$) ethanol solution for 20 hours. Both

electrochemically treated and untreated samples were compared by contact angle measurements. After electrochemical removal of the oxide, the thiol groups bind directly to the Ni surface. The advancing contact angle with water was ~110° and for the untreated Ni samples, where the oxide layer prevents binding of the thiol to the Ni surface, it was less than 50°. The big difference in the contact angle measurement indicates the different affinity of the thiol to the surface when electrochemically treated and untreated, as shown in Figure S2.

Figure S2: Contact angle images for electrochemically treated and untreated Ni surface after absorption of 1-Dodecanethiol monolayer.

AFM measurements

The conductive AFM experiments were carried out under a nitrogen purge to reduce undesired oxidation reactions. The conducting AFM probe was Pt-coated Si with a Ti adhesion layer (Mikromasch, NSC36/Ti-Pt). The details of the conductive AFM measurements were described previously.[4,5]

After the hybridization of the DNA on the Ni surface, a large topographic scan was performed to establish the density of the GNPs before performing the I-V measurement. Following the initial scan, a desired area was zoomed, and a custom script was used to ensure that the AFM tip measures I-V curves on the selected GNP.[4,5] As an example, in Fig. S3A, a 650x650 nm^2 image of the 40 bp DNA sample shows ~ 70 GNPs. The zoom of this image is shown in Fig S3B. The height of the bright dots are shown in Figure S3C

to be 10±2 nm, which fits the diameter of the GNPs. The larger dots seen in the image are clusters and were not used for analysis.

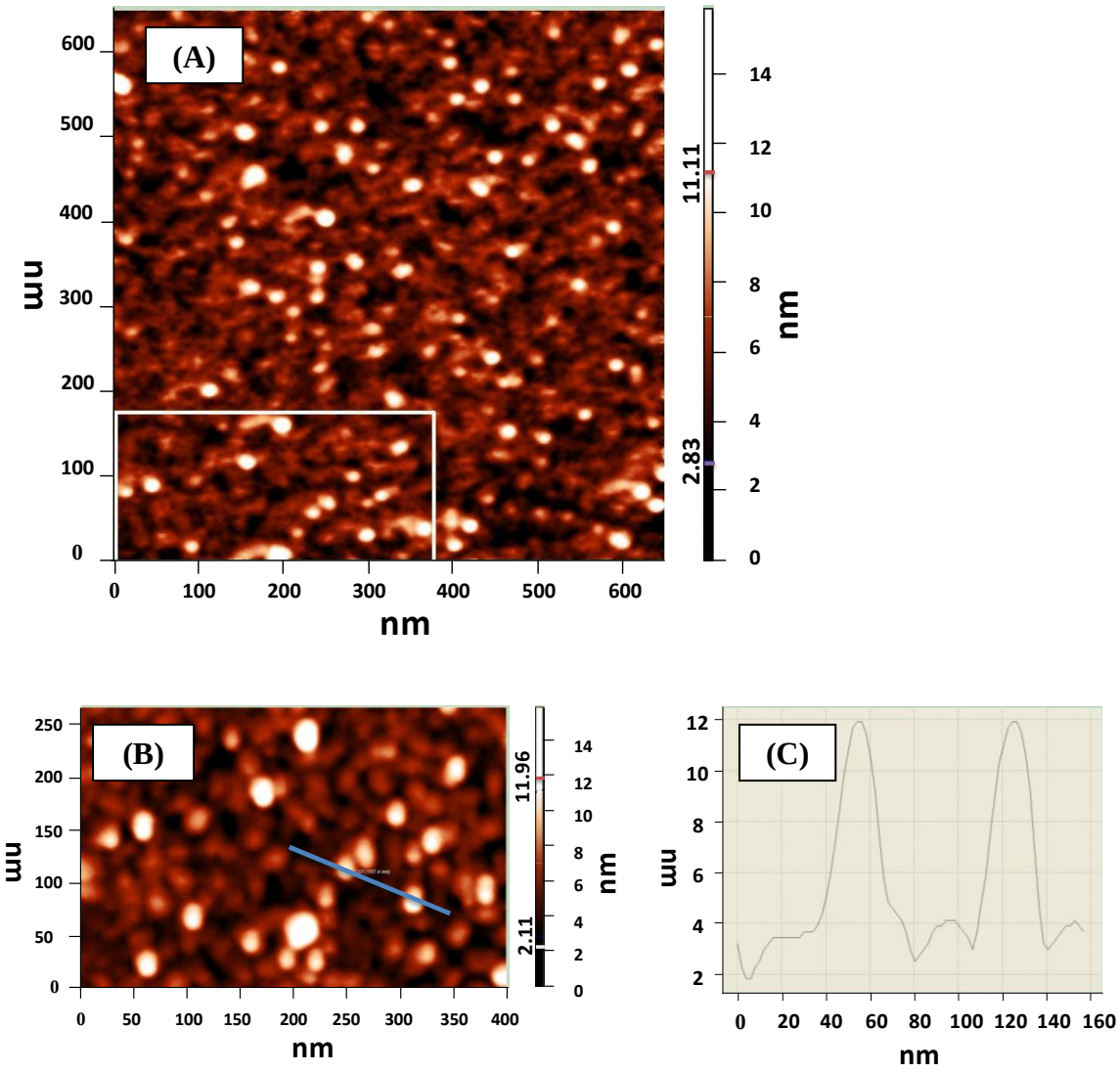

Figure S3: (A) AFM scan on a 40 bp sample by tapping mode covering a 650x650 nm^2 area. (B) A small area from (A) marked as a white rectangle was zoomed out (C) The height of the bright dot shows an average value 10±2 nm.

Conductivity of the AFM tip checked on the clean Au surface:

Before the I-V measurement on the gold nanoparticles, the conductivity of the tip used in the measurements was always checked on a clean Au surface. Figure S4 shows the I-V curve obtained from the tip on the Au surface. The curve indicates good ohmic contact

and the resistance is ~1.1x10^7 Ω, which is the value of the limiting resistor used to avoid high currents, which destroy the conductive tip coating.

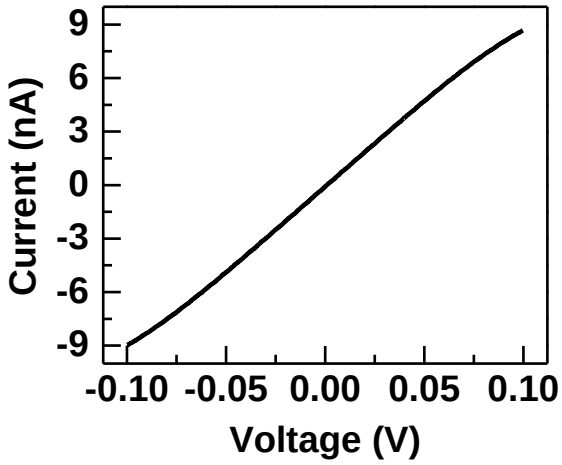

Figure S4: The conductivity of the AFM tip checked on clean Au surface before the measurements.

	base pairs	up	down	no
Ni substrate	26	61	104	/
	40	77	72	40
	50	118	113	116
Au substrate	40	91	81	/

Table S1: The amount of the measurements of 26, 40 and 50 base-pair (bp) long dsDNA, exposed to a magnet pointing up, down and no magnet on Ni or Au substrate.

Table S1 shows the number of measurements conducted for each type of sample with 26 bp, 40 bp or 50 bp dsDNA adsorbed on Ni substrate with magnet up and down and no magnet, as well as the control experiment of 40 bp dsDNA adsorbed on Au substrate with the magnet pointing up and down.

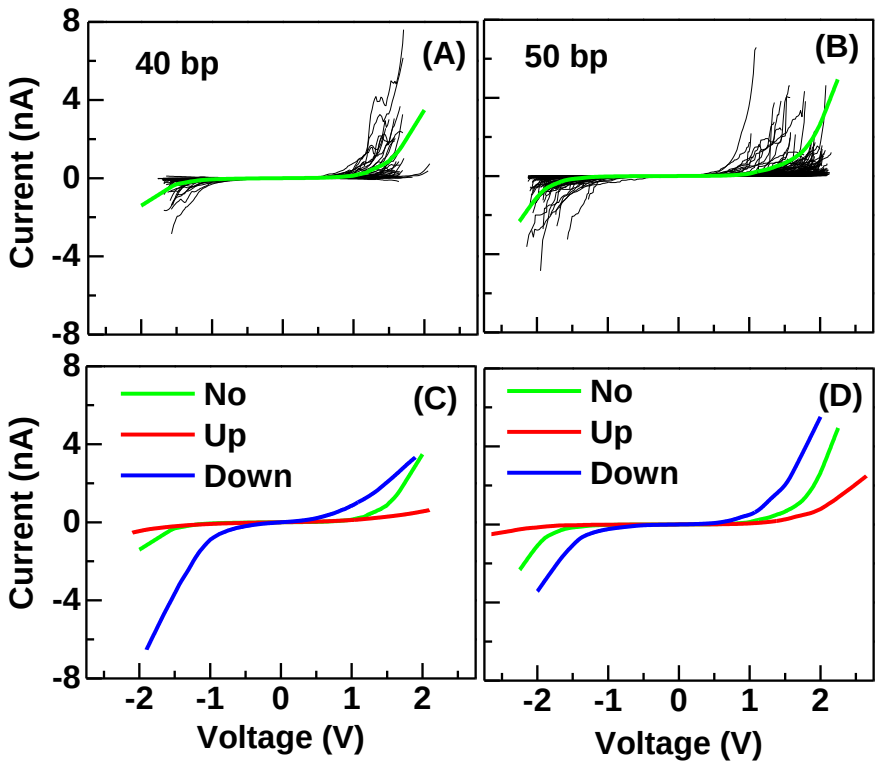

Figure S5: Current vs. voltage curves obtained for the (A) 40 and (B) 50 bp long DNA oligomers adsorbed on Ni when there is no magnet. The average current obtained for (C) 40 bp and (D) 50 bp oligomers studied with no magnetic (green), and with the magnetic field pointing up (red) or down (blue).

Figure S5(A) and S5(B) shows the I vs. V curves obtained for 40 and 50 bp DNA that without magnet. And the average of the current of tens of measurements for the 40 bp and 50 bp oligomers with no magnetic and the magnetic field is pointing up or down were put together in Fig. S5(C) and Fig. S5(D) respectively. It proves that the current without a magnetic field is the average current obtained with the magnetic field pointing up and down.

Control experiments

For verifying the effect of the chirality, control experiments were performed with 1, 9-nonanedithiol (DT), a non chiral monolayer, adsorbed on Ni. The samples were prepared by immersing an electrochemically cleaned Ni electrode in a methanolic solution of 1 mM DT for 20 hours. [6] The samples were then rinsed with ethanol and dried with N_2. One set of such samples was measured as is, and another set was incubated with GNPs. The GNPs were adsorbed by immersion in the GNP solution in analytical toluene (99.8%, Frutarom) for 4 hours. The samples were then rinsed and sonicated in toluene to remove any excess GNPs that were not covalently attached. The sample was then dried by a dry N_2 flow. Since the alkane thiol binds strongly to the Ni surface, a very dense coverage of Au NPs on Ni via dithiol linker was observed, as shown in Figure S6. The Au nanoparticles used here had an average diameter of ~5 nm. Conductive AFM measurements were performed on these samples. Figure S7A shows the statistics obtained for all measurements when the current in each scan is integrated between -0.5 V to +0.5 V. There is a nearly linear dependence of the current on the voltage in this voltage range as shown in Figure S7. The average resistance and standard deviation for magnetic field pointing up and down is $1.2\pm0.3\text{x}10^8$ Ω and $1.1\pm 0.3\text{x}10^8$ Ω respectively. This resistance of 1, 9-nonanedithiol is consistent with the results reported previously.[7] The resistivity does not depend on the direction of the magnetic field.

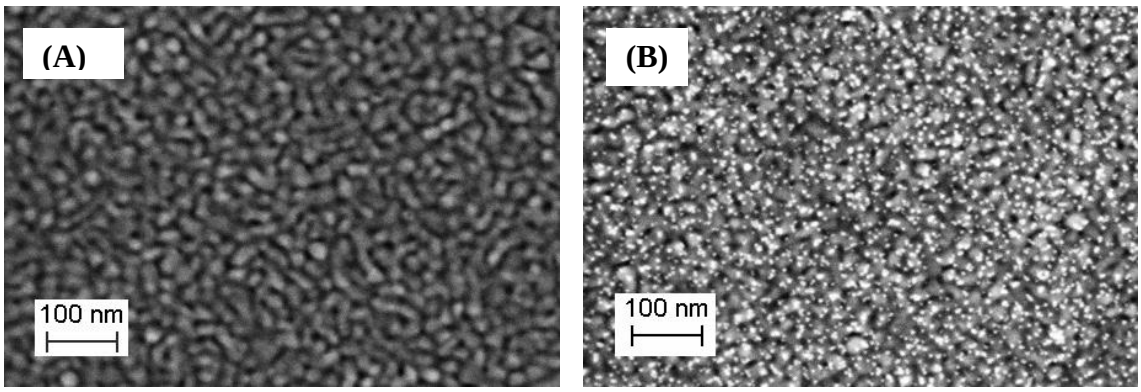

Figure S6: SEM Images (A) DT coated Ni (B) Ni coated with a DT monolayer and GMPs (5 nm diameter)

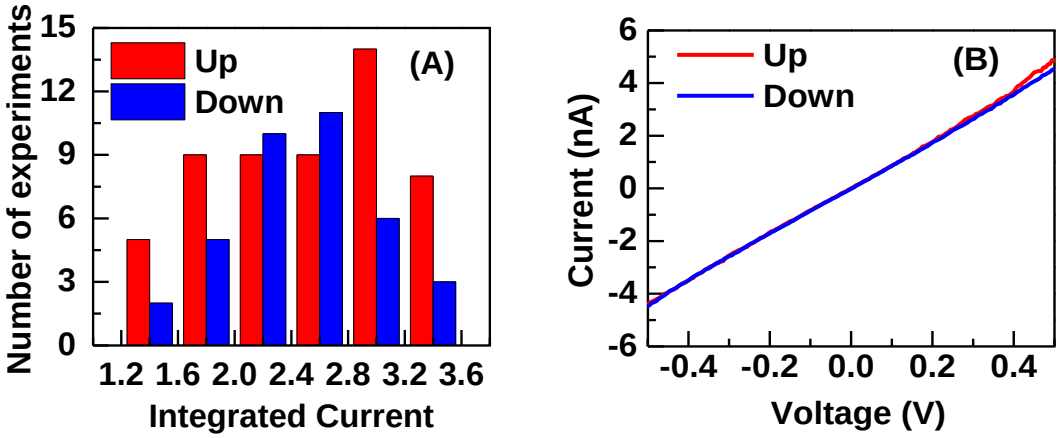

Figure S7: Current characteristics for constructs using 1.9-nonanedithiol (DT) linker. (A) Statistics for the current integrated between -0.5 V to 0.5 V for magnet pointing up (red) or down (blue). (B) Typical I versus V curves observed for GNPs/DT/Ni.

References

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