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Construction of highly conductive nanowires on a DNA template

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We present measurements of the electrical conductivity of metallic nanowires which have been fabricated by chemical deposition of a thin continuous palladium film onto single DNA molecules to install electrical functionality. The DNA molecules have been positioned between macroscopic Au electrodes and are metallized afterwards. Low-resistance electrical interfacing was obtained by pinning the nanowires at the electrodes with electron-beam-induced carbon lines. The investigated nanowires exhibit ohmic transport behavior at room temperature. Their specific conductivity is only one order of magnitude below that of bulk palladium, confirming that DNA is an ideal template for the production of electric wires, which can be utilized for the bottom-up construction of miniaturized electrical circuits. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1338967]

Building nanoscale structures with DNA is a focus of current research, stimulated by the enormous progress in utilizing DNA either for the controlled self-assembly of molecularly designed nanostructures,[1–7] or as template for thoroughly engineered inorganic structures.[6,8–11] Nevertheless, the construction of electronic circuits based only on native DNA remains problematic, mainly due to the high resistance of DNA that diminishes its potential applications in this regard.[12–18] Recently, Braun and co-workers presented a new approach by fixing DNA between two contacts and utilizing it as template for the construction of a silver nanowire.[6] This technique uses the molecular recognition properties of the molecule for the defined buildup of a nanostructure and installs its electrical functionality by the directed construction of a metallic wire on the biotemplate. However, the reported 100 nm thick silver wires displayed a electrical conductivity with a nonconducting gap for small bias voltages. Here, we report the production of nanowires showing ohmic transport behavior, which have been fabricated by direct growth of palladium on a single DNA molecule. For nanowires with a diameter above 50 nm, the specific conductivity is only one order of magnitude below that of bulk palladium. These investigations demonstrate that metallized DNA molecules can provide high conductive elements in a DNA-based circuitry.

In our experiment, we used metallized, linear λ-DNA molecules, 48 502 base pairs in length, to connect two gold electrodes several micrometers apart, with the whole assembly exhibiting an overall resistance well below 1 kΩ. DNA metallization is accomplished in a two-step chemical deposition of palladium,[10,11,19,20] involving

(a) activation of the template by treatment with Pd(II) complexes, which in part bind on the DNA strands,[21,22] and

(b) subsequent reduction of the complexes to form metallic clusters.

In a typical experiment a Pd solution was prepared by dissolving 5 mg of $Pd(CH_3COO)_2$ in 1 ml HEPES buffer (pH 6.5, 10 mM) by placing it in an ultrasonic bath for 2 min. Afterwards it was centrifuged for 5 min at 2000 g to obtain a saturated solution and to settle all undissolved particles. The Pd solution was diluted 1:8 with buffer solution. A 2 μl drop of DNA solution (0.1 mg/ml, λ-DNA, New England Biolabs) was placed onto a gold contact structure. The positioning of the DNA strands between the contacts is obtained by taking advantage of a simple, but powerful physical alignment process. The capillary forces applied by the receding front of the evaporating drop containing the DNA molecules are used to align the latter perpendicularly to the direction of the drying front.[23,24] Some of them attach to the surface and are not going to be removed by the subsequent treatment. Then, a 25 μl drop of the Pd solution was placed onto the sample with the aligned DNA strands and reacted for 2 h at ambient conditions. Finally, a 10 μl drop of reduction solution containing 2.5 gl^{-1} sodium citrate, 2.5 gl^{-1} of aqueous 85% lactic acid solution and 0.25 gl^{-1} dimethylamine borane with pH 7.4 was added to initiate cluster growth. The samples were rinsed carefully afterwards with aqua dest to avoid homogeneously grown clusters to settle down on the contact structure. The already grown cluster on the DNA can be developed by placing another drop of palladium solution on the sample and adding reducing agent, etc.

Initially, separated clusters are formed on the linear DNA template during the reduction process[10,11] [Figs. 1(a) and 1(b)] which is in close analogy to our observations for the growth of palladium and platinum clusters on protein templates such as bacterial surface layers and microtubules.[19,20] These clusters serve as a catalytic surface for the further reduction of palladium leading to a transition

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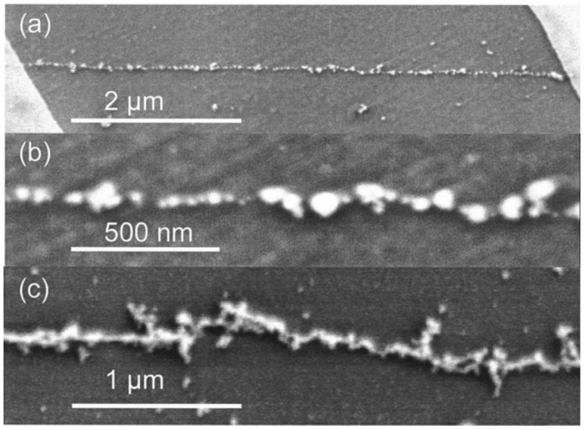

FIG. 1. Low voltage (1 kV) scanning electron microscope image of different stages of the metallization process. (a) Linear chain of separated palladium clusters connecting two gold contacts; (b) magnification of (a) showing clusters with diameters up to 40 nm; (c) continuously coated DNA strand after one development step with a diameter larger than 40 nm. The small dendrites perpendicular to the strand arise from the growth of the metal film on the template, that is driven by random processes.

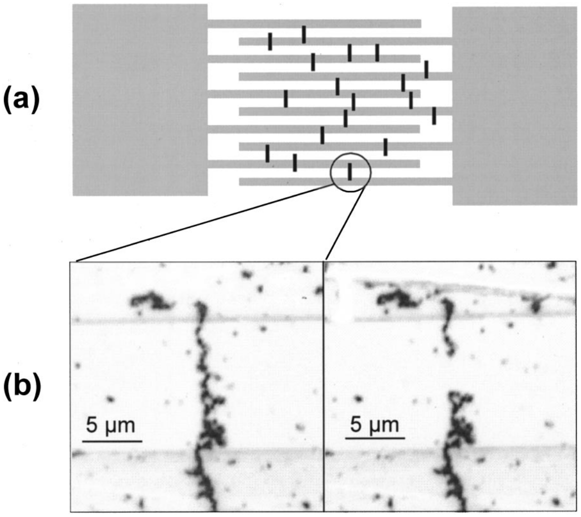

FIG. 2. (a) Sketch of parallel oriented nanowires (vertical black lines) on the comb-like gold contact structure (gray) showing five pairs of contact lines. We used different types of samples from 5 to 10 μm spacing between the gold contact lines. The alignment of DNA was achieved before metallization by placing a drop of DNA solution on the contact structure and removing it with filter paper perpendicular to the contact lines; (b) laser scanning microscope image of a palladium wire. The nanowire bridges two gold lines that are 10 μm apart. The left-hand side image is taken before and the right-hand side one after the cutting of the nanowire using a standard micromanipulator with etched tungsten tips.

from separated clusters into a continuous metal coating at a minimum film thickness of about 20 nm after one or two development steps [Fig. 1(c)].[11] Transmission electron microscopy shows that the metal films exhibit a granular structure with grain sizes of 2–4 nm. By varying the number of development steps, we are able to reproducibly build chains of separated clusters through to wires with a continuous metal coating. Thus, the approach presented here enables a tunable metallization of DNA. In this letter, we will focus on the electrical properties of continuously coated wires, since they provide the reasonably high conductivity necessary for electronic applications.

The described procedure allows the deposition of a large number of nanowires with parallel orientation onto a comb-shaped contact structure, where a number of wires bridge two adjacent electrodes in a random manner [Fig. 2(a)], thus providing a two-terminal measurement of an ensemble of nanowires all connected in parallel. In this configuration, the resistance R of one individual nanowire can be easily determined by breaking a particular wire by means of a micromanipulation device integrated in an optical microscope [see Fig. 2(b)] and measuring simultaneously the overall resistance of the system before and after cutting, R_b and R_a, respectively. In this case, the resistance of the wire removed is given by $R=R_aR_b/(R_a-R_b)$. The main advantage of the experimental approach described here is that it allows the investigation of a large number of wires generated in a single preparation step, and thus, enables the accumulation of statistically relevant datasets in a relatively short time.

We investigated more than one hundred nanowires and all showed ohmic behavior at room temperature, indicating that a diameter of about 50 nm is sufficient to achieve a continuous metallization of the DNA. However, although an almost linear dependence of the resistance on the spacing between adjacent Au electrodes was observed, indicating that the wire resistance scales with its length, initially none of the wires exhibited a resistance below 5 kΩ—even on the assembly of relatively thick nanowires (diameters up to 200 nm). This behavior, caused by contact resistances between the palladium nanowire and the Au electrodes, could be considerably improved by deposition of electron-beam-induced carbon lines[25–27] written over the very ends of the wires, where they interface the Au electrodes. The impact of this additional pinning is twofold. First, the wires are mechanically fixed to the Au pads, and second, the deposition and electron beam treatment lowers the contact resistance. The pinning proved to be extremely effective. In most cases the observed resistance drop after pinning was of the order of 5 kΩ, yielding overall two-terminal resistances below 1 kΩ, and thus, maximum contact resistances of several hundred Ω.

Two-terminal $I-V$ curves of single nanowires were taken after removing all other wires from the sample. Figure 3 shows such a particular wire with a continuous Pd coating around 50 nm in diameter. The corresponding $I-V$ curve is given in Fig. 4. We find ohmic behavior with a resistance of only 743 Ω. Cutting of this nanowire resulted in an insulating sample, proving that the measured conductance was indeed caused by this particular nanowire. The inset of Fig. 4 shows that the linear current–voltage dependence can be observed for bias voltages down to 1 μV. No evidence of a nonconducting region[6] or Coulomb blockade behavior,[28] was found at room temperature.

The minimum specific conductivity, σ_1, of the nanowire shown in Fig. 3 can be evaluated by neglecting the remaining contact resistances between the wire and the Au electrodes. We calculate $\sigma_1 \approx 2\times 10^4\ \mathrm{Scm}^{-1}$ for a wire length of 6.5 μm and an average diameter of about 50 nm. This value is less than one order of magnitude smaller than that of bulk palladium giving clear evidence of the metallic character of the wire conductivity. Furthermore, we estimated the specific conductivity, σ_2, of a disordered Pd wire within the Drude model[29] assuming an electron mean free path of about 2 nm.

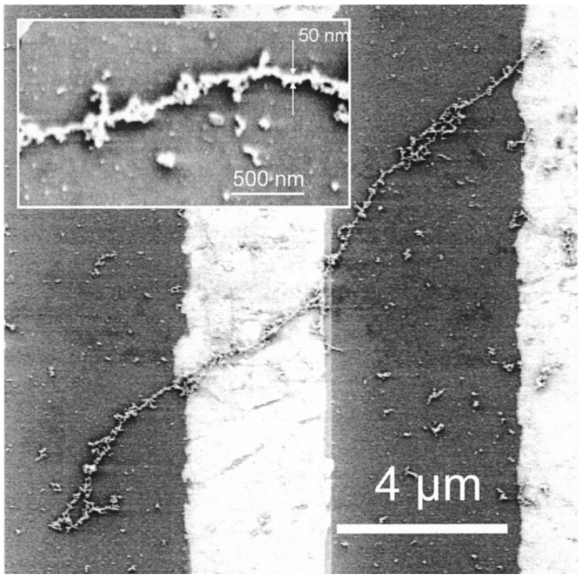

FIG. 3. Low voltage (1 kV) scanning electron microscope image of a single palladium metallized DNA strand with a length of ~16 μm corresponding to the length of a λ-DNA molecule. The right-hand side of the strand connects two gold electrodes over a SiO_2 substrate. The inset shows a magnification of the middle part with a diameter of 50 nm.

The latter value corresponds to the typical grain size of the Pd metallization film and provides an upper estimate of the electron mean free path assuming electron scattering at grain boundaries to be the dominant mechanism. These considerations yield $\sigma_2 \approx 10^4$ Scm^{-1} in agreement with σ_1 calculated from experimental data. From these calculations we conclude that the remaining contact resistance does not dominate the two-terminal resistance measured in our experiment, illustrating the enormous benefit of the pinning procedure.

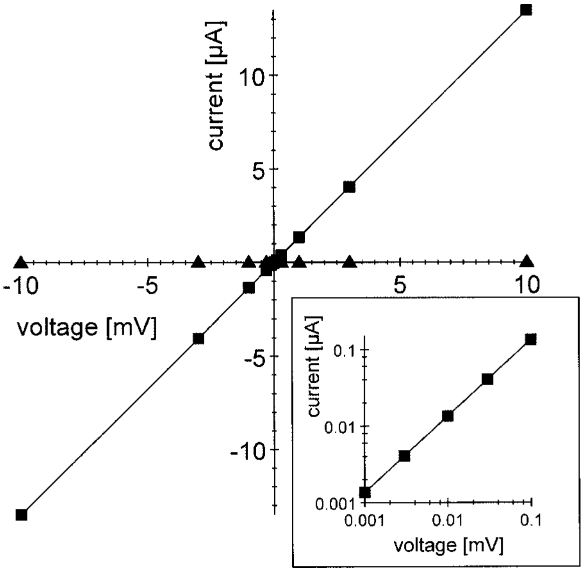

FIG. 4. Two-terminal current–voltage curves of the single, pinned nanowire shown in Fig. 3 before (■) and after (▲) cutting, taken with a patch-clamp amplifier (EPC9, Heka, Germany). The wire resistance is 743 Ω corresponding to a minimum estimated specific conductivity of $\sigma_1 \approx 2\times10^4$ S cm^{-1}. The inset shows the ohmic $I-V$ characteristic of the nanowire down to 1 μV. After cutting, the sample was insulating.

In conclusion, we have demonstrated the assembly of highly conductive palladium nanowires on a DNA template. The estimated specific conductance of the nanowires is only one order of magnitude smaller than for bulk palladium. Thus, the present study provides a step towards realistic electronic elements based on biological templates by showing the template capabilities of DNA. Moreover, the metallization of the DNA templates opens new possible applications of DNA wiring at elevated temperatures where native, uncoated DNA molecules are no longer stable.

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[1] N. C. Seeman, Annu. Rev. Biophys. Biomol. Struct. **27**, 225 (1998).
[2] A. P. Alivisatos, K. P. Johnsson, X. Peng, T. E. Wilson, C. J. Loweth, M. P. Bruchez, and P. G. Schultz, Nature (London) **382**, 609 (1996).
[3] C. A. Mirkin, R. L. Letsinger, R. C. Mucic, and J. J. Storhoff, Nature (London) **382**, 607 (1996).
[4] R. Elghanian, J. J. Storhoff, R. C. Mucic, R. L. Letsinger, and C. A. Mirkin, Nature (London) **277**, 1078 (1997).
[5] R. F. Service, Science **277**, 1036 (1997).
[6] E. Braun, Y. Eichen, U. Sivan, and G. Ben-Yoseph, Nature (London) **391**, 775 (1998).
[7] C. A. Mirkin, MRS Bull. **25**, 43 (2000).
[8] J. L. Coffer, S. R. Bigham, X. Li, R. F. Pinizzotto, Y. Rho, G. Young, R. M. Pirtle, and I. L. Pirtle, Appl. Phys. Lett. **69**, 3851 (1996).
[9] T. Torimoto, M. Yamashita, S. Kuwabata, T. Sakata, H. Mori, and H. Yoneyama, J. Phys. Chem. B **103**, 8799 (1999).
[10] W. Pompe, M. Mertig, R. Kirsch, R. Wahl, L. C. Ciacchi, J. Richter, R. Seidel, and H. Vinzelberg, Z. Metallkd. **90**, 1085 (1999).
[11] J. Richter, R. Seidel, R. Kirsch, M. Mertig, W. Pompe, J. Plaschke, and H. K. Schackert, Adv. Mater. **12**, 507 (2000).
[12] M. R. Arkin, Science **273**, 475 (1996).
[13] Y. Okahata, T. Kobayashi, K. Tanaka, and M. Shimomura, J. Am. Chem. Soc. **120**, 6165 (1998).
[14] J. Jortner, M. Bixon, T. Langenbacher, and M. E. Michel-Beyerle, Proc. Natl. Acad. Sci. U.S.A. **95**, 12759 (1998).
[15] E. Meggers, M. E. Michel-Beyerle, and B. Giese, J. Am. Chem. Soc. **120**, 12950 (1998).
[16] P. J. de Pablo, P. Moreno-Herrero, J. Colchero, J. G. Herrero, P. Herrero, A. M. Baró, P. Ordejón, J. M. Soler, and E. Artocho, Phys. Rev. Lett. **85**, 4992 (2000).
[17] P. T. Henderson, D. Jones, G. Hampikian, Y. Kann, and B. G. Shuster, Proc. Natl. Acad. Sci. U.S.A. **96**, 8353 (1999).
[18] D. Porath, A. Bezryadin, S. de Vries, and C. Dekker, Nature (London) **403**, 635 (2000).
[19] M. Mertig, R. Kirsch, W. Pompe, and H. Engelhardt, Eur. Phys. J. D **9**, 45 (1999).
[20] M. Mertig, R. Kirsch, and W. Pompe, Appl. Phys. A: Mater. Sci. Process. **196**, 723 (1998).
[21] J. Duguid, V. A. Bloomfield, J. Benevides, and G. J. Thomas, Jr., Biophys. J. **65**, 1916 (1993).
[22] G. B. Onoa, G. Cervantes, V. Moreno, and M. Prieto, Nucleic Acids Res. **26**, 1473 (1998).
[23] A. Bensimon, A. Simon, A. Chiffaudel, V. Croquette, and F. Heslot, Science **265**, 2096 (1994).
[24] D. Bensimon, A. Simon, V. Croquette, and A. Bensimon, Phys. Rev. Lett. **74**, 4754 (1995).
[25] H. König and G. Helwig, Z. Phys. **129**, 491 (1951).
[26] A. N. Broers, W. W. Molzen, J. J. Cuomo, and N. D. Wittels, Appl. Phys. Lett. **29**, 596 (1976).
[27] A. Bechtold, M. Henny, C. Terrier, C. Strunk, C. Schönenberger, J.-P. Salvetat, J.-M. Bonard, and L. Forro, Appl. Phys. Lett. **73**, 274 (1998).
[28] H. Grabert and M. H. Devoret, *Single Charge Tunneling* (Plenum, New York, 1992).
[29] C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1953).