Applied Surface Science 255 (2009) 9647–9651

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Photo-induced synthesis of DNA-templated metallic nanowires and their integration into micro-fabricated contact arrays

Christiane Erler, Katrin Günther, Michael Mertig *

BioNanotechnology and Structure Formation Group, Max Bergmann Center of Biomaterials and Institute of Materials Science, Technische Universität Dresden, D-01062 Dresden, Germany

ARTICLE INFO

Article history:
Available online 23 April 2009

PACS:
62.23.Hj
81.07.Pr
81.16.DN
87.14.gk

Keywords:
Bottom-up synthesis
Nanowires
DNA templating

ABSTRACT

We report the synthesis of metallic nanowires accomplished by site-specific integration of single DNA duplexes into micro-fabricated contact arrays and their subsequent selective metallization. DNA interconnects between metallic contacts are formed by tethering the ends of DNA molecules, stretched in hydrodynamic flow into a linear conformation, at different gold contact pads via thiol functional groups. To transform the DNA interconnects into metallic cluster chains or nanowires, we use an electroless metal deposition technique where platinum ions bound along the DNA molecules from a salt solution are reduced to metallic clusters of less than 10 nm in diameter by applying UV light.

1. Introduction

Novel approaches to the controlled bottom-up fabrication of advanced nanostructures increasingly involve synthesis routes that make use of the unique self-assembly capabilities of biomolecules [1–3]. In particular, DNA can be considered as basic building block for nanostructure fabrication because it provides unique self-recognition properties. The specific Watson–Crick base pairing allows programming its intra- and intermolecular associations, and consequently, to build-up relatively complex, artificially designed supramolecular structures [4–7]. Moreover, DNA constitutes an ideal template for the organization of metallic and semiconductor particles into wire-like assemblies [1,8–14].

Here we report a two-step procedure for the DNA-templated, in-place synthesis of metallic nanowires in micro-fabricated contact arrays. In the first step, functionalized DNA duplexes are site-specifically integrated into the contact array which involves local attachment of the DNA ends at the metallic contact pads and stretching of the molecule into a linear, 'wire-like' conformation by applying hydrodynamic flow. Although in the past a large number of experiments have been performed to measure the electrical conductance of native DNA duplexes, this subject is still matter of controversial scientific discussion [15]. Today it is not known, under which conditions DNA can provide conductance over distances larger than 100 nm which so far prevents the direct use of native DNA as molecular wire. To overcome this situation, in a second step the DNA duplexes assembled into complex networks are used as template for a selective deposition of metal to form conductive nanowires. Selective metal deposition can readily be obtained by electroless metal deposition where dissolved metal salt complexes are chemically reduced in the presence of DNA duplexes [1,8,9,11,16]. Thereby, the challenge is to control the nucleation kinetics, because metal clusters naturally nucleate homogeneously in the solution as well as heterogeneously at the template. Recently it has been shown that the homogeneous nucleation channel can be sufficiently suppressed when the efficient nucleation centres have been formed along the DNA molecules by incubating the DNA in the metal salt solution prior to the chemical reduction [8,9,11]. Here we present a different approach for the in-place metallization of surface-tethered DNA molecules where platinum ions bound to the DNA molecules are reduced to metallic clusters by exposure with UV light [17]. The size and distribution of clusters formed along the DNA molecules are investigated by atomic force microscopy, demonstrating that metallic clusters of homogeneous size grow on the DNA template integrated between the contact pads. By means of this two-step

* Corresponding author. Tel.: +49 0 351 463 39404; fax: +49 0 351 463 39401.
E-mail address: michael.mertig@nano.tu-dresden.de (M. Mertig).

0169-4332/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2009.04.127

procedure, parallel processing of complex patterns of metallized DNA interconnects can be performed and also large-scale applications are conceivable.

2. Experimental

Patterning of metal films by optical lithography has been applied to prepare interdigital micro-electrode arrays on glass slides. The metal films were prepared by evaporating 50 nm of gold on top of a 3 nm thick chromium adhesion layer. The micro-patterned electrodes are 2 μm wide and separated by 2 or 4 μm in the center of the interdigital array. The electrode distances at the brinks of the array correspond to 6, 8 and 10 μm. The gold pads were cleaned by immersing them for 20 s into fuming nitric acid (100%; Merck) and then for 1 min into a neutralization bath (hydrogen peroxide (30 wt% in water; Merck), ammonia solution (25 wt% in water; Merck), and deionised water in the ratio of 1:1:5).

After rinsing in deionised water, the structures were immediately installed into a home-made open flow cell (Fig. 1) and covered with 200 μl of HEPES buffer. The flow cell is mounted into an inverted optical microscope (Axiovert 200M, Carl Zeiss) equipped with an oil immersion objective (100×, N.A. = 1.45). Two micro-capillaries are mounted from above to accomplish fluid flow over the sample surface by means of a peristaltic pump (Watson Marlow). The advantage of this experimental set-up is the possibility of flexible and accurate positioning of the two micro-capillaries inside the fluid cell at variable lateral position and height by means of a micro-manipulation system (Luigs & Neumann) enabling an easy control of the direction of flow relative to the mounted electrode array.

For the binding experiments, we used λ-phage DNA molecules (48 502 bp long, corresponding to 16.2 μm contour length; New England Biolabs). To bind the two ends of the molecule specifically to the micro-patterned gold electrodes, the 12-bases long sticky ends on both sides of the λ-phage DNA were filled with nucleotides using a modified S^4TTP nucleotide (4-thiothymidine-5′-triphosphate; tebu-bio) which provides a thiol group for binding the modified DNA ends covalently to the gold contacts [18]. The functionalization was carried out in a Klenow polymerization reaction with dATP, dCTP, dGTP (Sigma), S^4TTP and the Klenow fragment (3′ → 5′ exo⁻, New England Biolabs). Then the DNA thiolated at both ends (T-DNA-T) was purified.

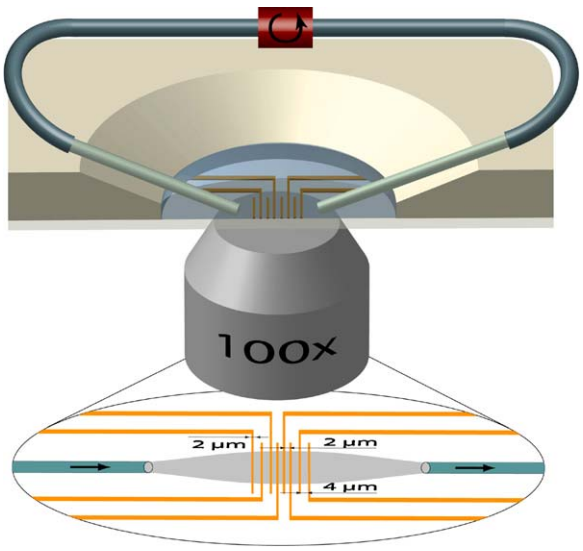

Fig. 1. Schematic viewgraph of the experimental set up. An open flow cell is mounted in an inverted fluorescence microscope. By means of a micro-manipulation system, micro-capillaries can be variably positioned above the interdigital electrode array, and thus, be used to create variable flow profiles in the cell. The electrode array is depicted enlarged in the lower part of the figure.

The incorporation of T-DNA-T into the interdigital electrode array was carried out in the open flow cell by positioning the micro-capillaries about 100 μm above the electrodes and flushing 2 μl of DNA solution (0.25 μg/μl) diluted in 50 μl PB 100 buffer over the contact array. The flow direction was chosen to be perpendicular to the long contact fingers of the interdigital electrodes (Fig. 1). To accomplish anchoring of T-DNA-T coils with one of their thiol-functionalized ends at the gold contacts, the DNA solution was pumped for 10 min back and forth over the contact array at low flow rate. After some of the molecules bound specifically to the gold contacts, the DNA solution was exchanged by the buffer solution and the flow rate was increased resulting in an uncoiling, and thus, stretching of the molecules in the direction of applied flow. As soon as the free thiolated end of the stretched molecule reaches the adjacent contact, it can bind via its thiol functional group there. When the flow is released, the molecule, now tethered with both ends to adjacent contacts, forms a linear DNA interconnect. To verify the formation of interconnects, the DNA molecules were stained after the stretching procedure with YOYO-1 (1.6 nM aqueous solution, Invitrogen). Fluorescence microscopy images were acquired with 300 ms exposure time using a cooled, 16-bit frame-transfer CCD camera (Visitron).

For the metallization of the assembled DNA interconnects, 25 μl of 100 mM $Pt(NO_3)_2$ solution were added to the buffer volume in the flow cell and, to allow Pt(II) ions to bind to the DNA, the cell was stored in a high humidity environment for 12 h in the dark. To our best knowledge, no specific studies addressing the binding behaviour of $Pt(NO_3)_2$ to DNA are reported so far. However, dissolved Pt^{2+} ions are expected to have an affinity to the aromatic N-sites of the nucleic base residues, but can also bind to the phosphate groups of the backbone of DNA [19]. As a consequence, long incubation times shall lead to a homogeneous, sequence-independent distribution of bound Pt ions along the DNA duplexes. After the incubation, the Pt ions were reduced to metallic Pt(0) by exposing the sample with UV light (254 nm, CL-1000 Crosslinker) for 10 min. After rinsing the structure in deionised water and blow-drying it with nitrogen, the resulting nanowires were imaged by atomic force microscopy (Digital Instruments) applying tapping mode in air.

In an additional microflow experiment, we investigated to which length a λ-phage DNA molecule can be stretched by hydrodynamic shear flow. To this end, we functionalized both ends of the λ-phage DNA with biotin in a similar way as described above but using a biotinylated nucleotide (biotin-11-dCTP; Invitrogen) instead of the thiol-modified nucleotide in the Klenow polymerization reaction [20]. The obtained B-DNA-B was attached with one end to the streptavidin-terminated glass surface of a microfluidic flow cell with a channel of 2.8 mm width, 13 mm length and 50 μm height. A streptavidin-conjugated CdSe quantum dot (Invitrogen) was attached to the free DNA end. The dependence of the extension of the molecule on the applied flow rate was measured by fluorescence microscopy at 605 nm emission wavelength.

3. Results and discussion

Without applying external forces, DNA duplexes form random coils in solution. Due to Brownian motion, the molecule undergoes fluctuations. When a B-DNA-B is tethered with one end to a substrate surface, the thermal fluctuations of the free molecule end can be studied by video fluorescence microscopy measuring the time-dependent positions of a quantum dot specifically attached to that end as described in Section 2 [20]. From the obtained data in the force-free case, intrinsic DNA properties like the end-to-end