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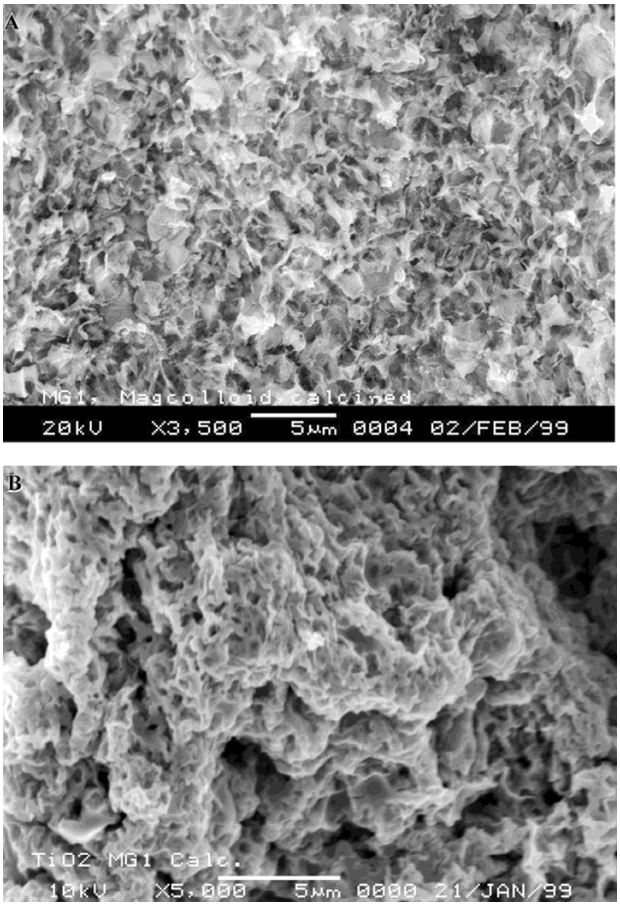

Fig. 6. A) SEM images of macrostructures prepared by infiltration of swollen MG1 gels with inorganic nanoparticles followed by calcination to remove the polymer template; A) magnetite and B) titania monoliths.

Preparation of Colloidal Sols: A magnetite colloid was prepared in alkaline solution according to the procedure published by Massart [11]. An aqueous solution containing 2.3 g (8.5 mmol) $FeCl_3 \cdot 6H_2O$ in 4 mL H_2O and 1.69 g (4.3 mmol) $Fe(NH_4)_2(SO_4)_2$ in 1 mL of 2 M HCl, was added to 50 mL of 1 M $(CH_3)_4NOH \cdot 5H_2O$. The resulting black suspension was stirred for 1 h at room temperature and then sonicated in an ultrasonic bath for 1 h. The colloid was then centrifuged at 20 000 g for 1 h. The supernatant was decanted and the slurry resuspended in 20 mL water by sonication before being passed through a 0.2 µm pore cellulose nitrate membrane.

A titanium dioxide sol was prepared by hydrolysis of titanium tetraisopropoxide under a nitrogen atmosphere following the procedure described by O'Regan et al. [12]. 25 mL of titanium tetraisopropoxide was mixed with 4 mL of isopropanol in a dropping-funnel under a nitrogen atmosphere. This mixture was added slowly over a period of 5 min to 150 mL of vigorously stirred double-distilled, deionized water in a 250 mL three-neck flask equipped with heater, thermometer and stirrer. Ten minutes after the final alkoxide addition, 1 mL of 69 % HNO_3 was added. The white hydrolysis mixture was then stirred for 8 h at 80 °C to remove the isopropanol, filtered through a 0.2 µm pore cellulose nitrate membrane, and sonicated for 1 h to produce a stable colloidal solution with a bluish-white coloration.

Preparation of the Composites and Method of Calcination: Typically, a sample of the sliced copolymer gel (ca. 5 mm thick) was added to the colloidal sol and left for the desired period of time. The colloid-loaded gels were removed, washed with water and allowed to dry in air. Thermogravimetric analysis (TGA) measurements were made using a NETZSCH STA 409EP machine. Samples were heated under air in an alumina crucible to a final temperature of 800 °C at a rate of 5 K/min. Large samples of the mineralized gels were calcined by heating to a temperature of 450 or 500 °C in a Carbolite furnace (type ELF11/6) at a heating rate of 1 °C min^{-1}.

Analytical Methods: The morphology of the copolymer gel in the water-swollen state was examined using a Jeol 6310 SEM equipped with a cryo-stage and energy-dispersive X-ray (EDX). A sample of the gel was rapidly frozen in liquid nitrogen and introduced into the SEM-chamber cooled to a temperature of ca. –180 °C. The stage was heated up to a temperature of ca. –90 °C to sublime the surface water. After cooling down to –180 °C, the sample was gold sputtered for 2 min. Routine imaging of the air-dried composite and calcined samples was conducted using a JEOL 5600 LV analytical SEM. A JEOL 1200EX TEM was used to investigate the colloid dispersions and crushed fragments of the composite and calcined samples. Magnetization curves were recorded using a LDJ Electronics vibrating sample magnetometer operating at room temperature.

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Nanoscale Palladium Metallization of DNA**

By *Jan Richter,* Ralf Seidel, Remo Kirsch, Michael Mertig, Wolfgang Pompe, Jens Plaschke,* and *Hans K. Schackert*

The attempt to use biomolecular systems in the investigation of the physics of nanostructures, combines two rapidly developing scientific fields and represents a promising approach for future nanotechnology. In particular, the combination of organic templates with nanosize metal clusters illustrates the capabilities of this approach. First, one can focus on the biological system and use the cluster as an additional tool for micromanipulation, sensing operations,

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etc.[1] Second, it is possible to use the technique of biotemplating to build defined inorganic nanostructures.[2–6] In this case the organic structure serves as a template for the formation of an inorganic system with the pattern of the template.

Among the biological molecules, deoxyribonucleic acid (DNA) is one of the most interesting template systems, because of its diameter of only 2 nm and the micrometer-long distribution of well-defined sequences of DNA bases. This structure makes it possible to create complex nanostructures by a building-up process using complementary DNA strands.[7] Furthermore, the DNA molecule exhibits poor electron transfer rates,[8] which result in very low conductance.[9] Therefore, it could serve as an isolating quasi-one-dimensional (quasi-1D) template for metallic cluster deposition.

Recently Braun et al.[4] realized a DNA-template-based silver nanowire around 100 nm thick and 15 μm long. The metallization was performed in three steps. First, the DNA was fixed between two electrical contacts. Then it was activated with a solution containing silver ions, which bind to the DNA bases. In the third step the DNA was metallized with silver using a standard photographic enhancement technique. The resulting nanowires showed a resistance of several mega-ohms as a result of the coagulation of silver, which leads to clusters with a diameter of 50 nm.

In this work we study the formation of nanoscale palladium clusters on a DNA template. Here chains of separated clusters and a continuous coating to give a metal nanowire are of equal interest. A well-defined cluster system with monodisperse, regularly aligned clusters of 1–5 nm diameter would allow investigations on single electron tunneling (SET) at room temperature.[10] SET oscillations can be observed when the Coulomb blockade energy is larger than the thermal noise. A rough estimate of the energies involved requires the cluster size $s < e^2/(2kT4\pi\varepsilon) = 27$ nm, with e being the electron charge, k the Boltzmann constant, T the temperature, and ε the dielectric constant. On the other hand, a continuous metal coating would be an interesting approach to producing metallic nanowires. Here, one advantage of a biomolecular template is the possibility of building small-scale network structures, such as nanoscale Aharonov–Bohm rings. These networks exhibit an interesting feature: interference effects of the electron wavefunction.[11]

In previous work we have shown that it is possible to grow nanoscale metal clusters on self-assembled protein structures using palladium (Pd) and platinum (Pt) complexes. So far, two biological systems have been studied: the formation of a 2D periodic structure of 2 nm Pt and Pd clusters on the bacterial surface layer of *Sporosarcia ureae*,[2] and the quasi-1D nickel metallization of microtubules,[3] a protein filament of the cytoskeleton.

In the work reported here the same technique of cluster deposition was applied for the metallization of λ-DNA. This was accomplished by activating the DNA with Pd ions and adding a reduction bath afterwards (for details see the Experimental section), leading to the formation of nanoscale Pd clusters on the DNA. Depending on the duration of the reduction process, well-separated Pd clusters become a quasi-continuous Pd film with a grain-like structure on the DNA.

Within a few seconds of the reduction agent being added, nanoscale clusters of Pd grow on the DNA (Fig. 1). The clusters, with a diameter of 3–5 nm, remain separated. When the duration of the reduction process is extended, Pd cluster aggregates are formed as a result of further deposition of metal. Here, the initially formed clusters serve as autocatalytic surfaces for further reduction of Pd ions. After 1 min quasi-continuous coverage is achieved, with cluster aggregates 20 nm in size (Fig. 2).

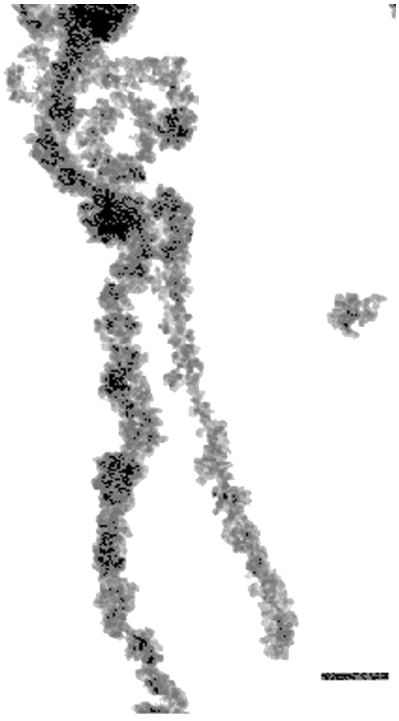

Fig. 1. TEM picture of a metallized DNA strand at an early stage of the metallization process. The formation of well-separated Pd clusters 3–5 nm in size is depicted (scale bar 20 nm).

In an aqueous solution DNA is not fixed to a surface. Therefore, it occasionally forms loops. During the metallization process these stochastic loops can become pinned and the resulting nanowire geometry reflects this loop fixation. One example of such a small-scale network is shown in Figure 2.

The up to 5 μm long nanowires observed (see inset in Fig. 2) have a quasi-continuous 20–40 nm thick Pd coating. Obviously, the metal deposition is connected with an embrittlement of the DNA. The contour length of metallized wires is always shorter than the 16 μm of native λ-DNA for two reasons. First, the binding of Pd complexes to DNA leads to bending of the DNA base planes during the activation process.[12] From atomic force microscopy (AFM) in-

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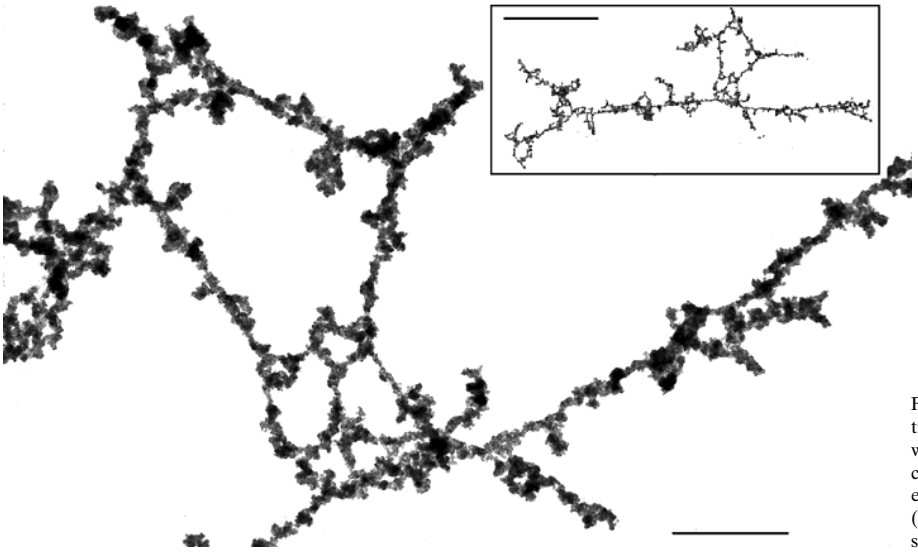

Fig. 2. Detail of a metallized DNA strand illustrating the small-scale networks of the nanowires. The alignment of clusters on the DNA can be seen, as well as the quasi-continuous coverage of the surface with cluster aggregates (scale bar 200 nm). Inset: The complete DNA strand (scale bar 1 μm).

vestigations it is known that this microscopic bending of base planes results in macroscopic shortening of the DNA.[13] Second, growth of cluster aggregates during the reduction process changes the mechanical properties of the strand dramatically. As a consequence the strand is embrittled and can break easily. This behavior is similar to the observed macroscopic deformation of microtubules as a result of cluster growth during metallization,[14] although their tube-like structure is considerably stiffer than that of DNA.

In a further step we investigated a possible way to metallize aligned DNA immobilized on a substrate. The alignment of DNA strands was achieved by controlled evaporation of a drop of DNA solution on a glass coverslip surface. Due to the liquid motion, strands are moved to the meniscus of the drop. When a DNA strand occasionally adsorbs at the surface, it will be pulled by the receding meniscus and deposited perpendicularly to it. This process leads to parallel orientation of the strands. It can be visualized by using fluorescence-labeled DNA (see inset in Fig. 3).

In a following step Pd acetate solution was placed on the glass substrate covered with aligned DNA. The adsorption of the DNA onto the glass surface is so strong that, once dried in, the strands will only be removed partially by the subsequent Pd solution treatment during the activation process. The reaction of DNA with Pd was monitored by quenching of the fluorescence signal in accordance with observations by Braun et al.[4] Finally the reduction bath was added.

Figure 3 shows Pd nanowires as a result of this treatment. From these observations we conclude that the described metallization method is suitable for immobilized DNA, which is an important practical aspect for future experiments on DNA fixed between electrical contacts.

In summary, we have demonstrated a method for the nanoscale Pd metallization of DNA by electroless deposition of a metal. The surface of the DNA was activated with

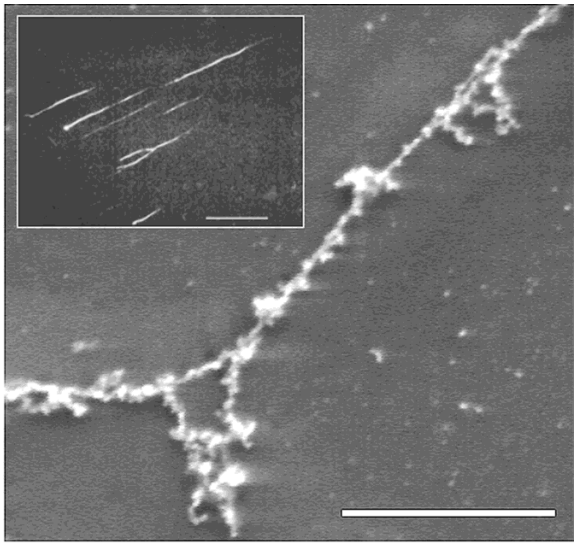

Fig. 3. SEM picture of a metallized DNA strand 40 nm thick on a glass surface. The DNA was aligned by evaporating a drop of DNA solution and metallized afterwards. For better visualization the sample was covered with 1 nm carbon (scale bar 1 μm). Inset: Parallel aligned fluorescence-labeled DNA strands before metallization (scale bar 10 μm).

Pd ions before a reduction bath was applied to form nanoscale clusters on the DNA. We observed different cluster sizes according to the duration of the reduction process. The initially grown metal clusters (3–5 nm) are, for the first time, on the same scale as the diameter of the DNA itself. Longer reduction times lead to a transition from these separated clusters to a quasi-continuous coverage of DNA with cluster aggregates 20 nm in size. The method leads to a structural transition from a nanostructure consisting of separated clusters to a quasi-continuous metal coating. This offers a way of studying the physical properties of novel mesoscopic systems.

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Experimental

Metallization of DNA in Solution: The DNA was metallized in a two-step procedure. In the first step, DNA was activated with Pd acetate. The Pd acetate solution was prepared by dissolving 10 mg of $Pd(CH_3COO)_2$ in 1 mL of distilled water and then 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 unresolved particles. The Pd acetate solution was mixed for 2 h with an equal amount of DNA solution (λ-DNA, New England Biolabs, 0.005 mg/mL in 10 mM Tris [tris(hydroxymethyl)aminomethane] buffer).

In a second step a reduction bath was added, which contained 25 $g\,L^{-1}$ sodium citrate, 25 $g\,L^{-1}$ of 85 % lactic acid aqueous solution, and 2.5 $g\,L^{-1}$ dimethylamine borane (DMAB). The pH was adjusted to 7.4 with NH_4OH. The ratio of DNA solution to reduction bath was 5:1. The reaction was monitored by extinction measurements (data not shown) and stopped by diluting the solution at least 50-fold with distilled water. Samples for transition electron microscopy (TEM) investigations (Philips CM 20 at 200 kV) were absorbed onto carbon-coated grids for 2 min and rinsed afterwards.

Metallization of Immobilized DNA: The metallization of immobilized DNA was carried out in a slightly different way. In the first step a drop of 1 ML fluorescence-labeled DNA solution (YOYO-1, Molecular Probes, Oregon, for 24 h) was placed on a glass coverslip. The drop evaporates in about 5 min, and alignment of DNA was observed during this process by fluorescence microscopy. After evaporation a drop of 100 µL Pd solution was placed onto the immobilized DNA. The drop was not allowed to dry in. After 2 h, an additional drop of 20 µL reduction bath was placed on the structure. All liquids were removed with filter paper after 5 min. For better contrast the sample was covered with a 1 nm carbon film before imaging and investigation in a scanning electron microscope (Zeiss Gemeni at 2 kV).

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Functional Membranes Containing Ion-Selective Matrix-Fixed Supramolecular Channels**

By *Uwe Beginn,* Gabriela Zipp,* and *Martin Möller*

Synthetic functional membranes, capable of selectively recognizing and transporting ions or molecules, represent a challenging target for preparative membrane science. The availability of such membranes might cause significant changes in industrial and laboratory praxis, since energy- and labor-intensive purification methods could be replaced by isothermal membrane processes. Their potential importance can be imagined by the fact that about 40 % of the energy consumption in chemical industry is used for distillation and recrystallization processes.[1] Highly selective membranes would also simplify numerous separation tasks or detection problems in the fields of biochemical, medical, or even environmental analytical technology.

Biological cells effect the extracellular exchange of matter by means of membrane-spanning transport channels, consisting of reversibly self-organized aggregates of functional proteins.[2] The channels localize the permeation path and, simultaneously, the transport process is protected against the environment. External factors hardly influence the transport mechanism or change the permeate while being transported. Selectivity emerges from the size of the transporter space and from the interactions between the permeate and the wall. Since the thickness of technical membranes (20–100 µm) far exceeds that of lipid bilayers (15 nm), biological channels cannot simply be copied.

Here we present a concept for incorporating functional channels into "thick" films based on the self-assembly of low-molecular-weight amphiphiles into very long, solid cylindrical aggregates. To enable supramolecular transport through the cylinders they should contain functional receptor units in their center. In order to fix them permanently to the membrane matrix, the outer rim of the cylinder is functionalized by polymerizable olefin groups. For the functional receptor groups we selected crown ether receptors, because of their polarity and alkali-metal selectivity.[3–5] In order to obtain stacks of the crown ethers we employed a concept developed by Percec et al.:[6] 2-hydroxymethyl-[1,4,7,10,13-pentaoxabenzocyclopentadecane]-3,4,5-tris[4-(*n*-dodecyl-1-oxy)benzyloxy]benzoate (DOBOB-CE) was found to form supramolecular columns in which the crown ether moieties were stacked parallel to the column axis, forming potential ion channels. The material showed ionic conductivity in its mesophase.[6]

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