Fabrication of Silver Nanowires by Selective Electroless Plating of DNA Stretched Using the LB Method

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Precise and uniform metallization of double-stranded DNA by the selective electroless plating method was investigated for the fabrication of nanowires. Cis-platin was bound to template DNA molecules and reduced to platinum which then catalyzed silver metal deposition. The DNA molecules combined with the platinum clusters were stretched and immobilized on a glass substrate using the Langmuir–Blodgett (LB) method. The electroless plating of the platinum-bound DNA molecules by the reduction of silver ions yielded uniform silver nanowires (ca. 50 nm in width and height) along the stretched DNA molecules. Conductive AFM measurements revealed that a high electric conductivity over a length of 6 μm from the edge of a micro electrode.

The fabrication of metal nanowires out of double-stranded DNA as template for metallization has attracted much attention from the view point of self-assembly manufacturing of custom-made nano-devices.[1] For the DNA-based fabrication of nanowires, some groups have suggested several methods, such as an arrangement of metal nanoparticles on DNA,[2] reduction of metal ion preadsorbed to DNA,[3] and electroless plating.[4] However, the number of experimental reports on conductivity measurements of DNA-based nanowires is very limited.[5] In order to prepare fine nanowires using DNA, the precise and uniform metal deposition that occurs only on stretched DNA molecules is a critical requirement. In this paper, we report the fabrication of fine silver nanowires out of stretched DNA molecules by using a selective electroless plating method. This method is a fundamental technique for the deposition of metal on a specific surface by the reduction of metal ions in the presence of a catalyst.

When DNA is used as a template for a selective electroless plating method, a catalyst for the electroless plating needs to be bound to the DNA prior to the electroless plating. For this purpose, we chose cis-platin as the catalyst precursor. Cis-platin is a platinum compound that forms covalent bonds with the seventh nitrogen atom of such purine bases as adenine and guanine of DNA.[6] The cis-platin bound to the DNA was reduced to platinum metal. The platinum deposited on DNA can act as the catalyst of the silver electroless plating. The experimental procedure of the selective electroless plating of stretched DNA was shown in Figure 1.

The DNA molecules combined with platinum were stretched and immobilized on a glass substrate using the Langmuir–Blodgett (LB) method. We have found that when a DNA-amphiphile polyion complex monolayer, which is formed at the air-water interface, was transferred to a glass substrate using the LB method, DNA molecules were immobilized on the glass substrate in a stretched configuration.[7] The LB method does not require any surface modification of the substrate (for example, amino silane coupling), which the "molecular combing"[8] method requires. The silver metal deposition of stretched platinum-bound DNA immobilized on the substrate was investigated.

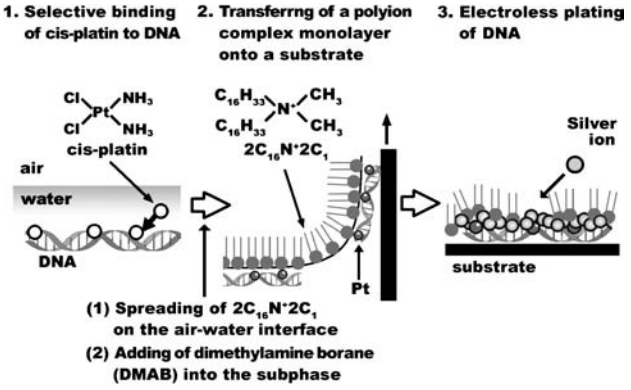

Figure 1. A scheme for the fabrication of silver nanowires by the selective electroless plating using stretched DNA molecules as template.

A DNA-amphiphile polyion complex monolayer was formed by spreading dihexadecyldimethylammonium bromide ($2C_{16}N^{+}2C_1$) (Sogo pharmaceutical Co., Ltd.) on a Tris-HCl buffer solution (pH 7.8 at 20 °C) of 1.0×10^{-8} M (in base pair) Lambda DNA (Nippon Gene Co., Ltd.), 2.5×10^{-6} M cis-platin (Wako Chemical Co., Ltd.) and selective fluorescence probe dye for DNA (YOYO-1 (Molecular Probe Co., Ltd.)) (if necessary). After the reduction of cis-platin to platinum by the addition of 10 mL of 25 mM dimethylamine borane (DMAB) (Wako Chemical Co., Ltd.) aqueous buffer solution into the subphase behind the barrier, the DNA-amphiphile polyion complex monolayer was transferred to a glass substrate at the surface pressure of 5 mN/m by the LB method. The fluorescence image of the transferred polyion complex monolayer shows that DNA molecules were stretched, though cis-platin was reduced in the subphase (Figure 2a). For an AFM measurement, the polyion complex monolayer was transferred to a mica substrate by the horizontal lifting method (the Langmuir–Schäfer method), since it could not be deposited on a mica substrate by vertical lifting method. A pearl necklace like structure was observed (the inset of Figure 2a). The height and width of the line was approximate 1 and 2-nm respectively, indicating that the lines corresponded to the stretched single molecules of DNA. The size of the dots along the DNA reached 2 nm in height and 5 nm in length. The absence of cis-platin in the subphase yielded a line structure without dots, indicating that the dots represent platinum clusters formed by the reduction of cis-platin.

Silver metal deposition on DNA was carried out by immers-

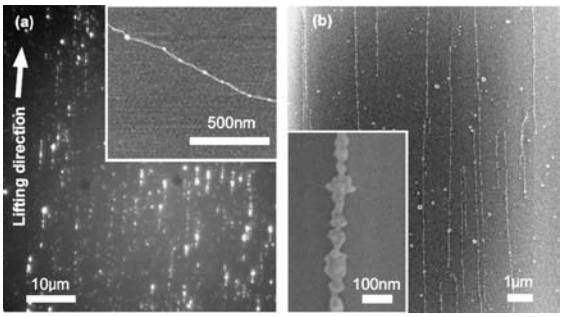

Figure 2. (a) A fluorescence image of a DNA-$2C_{16}N^{+}2C_1$ complex monolayer with reduced cis-platin. The inset shows the AFM image of the complex monolayer transferred onto mica by a horizontal lifting method. The bright dots indicate platinum particles. (b) SEM images of a DNA-$2C_{16}N^{+}2C_1$ complex monolayer after silver electroless plating. The inset shows a magnified view of the line structures obtained.

ing the glass substrate on which stretched DNA with platinum clusters was immobilized by the LB method into a silver electroless plating solution,[9] which was comprised of 0.03 M silver nitrate, 1.22 M ammonia solution, 0.5 M acetic acid and 0.1 M hydrazine (all reagents were purchased from Wako Pure Chemical Co., Ltd.) Then the glass substrate was washed using the ultrapure water and dried by blowing of nitrogen gas. The SEM image of the silver-deposited surface was shown in Figure 2b. Uniform silver nanowires (ca. 50 nm in width and height) along the stretched DNA molecules were observed. The length of almost silver nanowires was 15–17 μm as same as the length of Lambda DNA. In the case where the electroless plating solution was used without a reducing reagent (hydrazine), no wire structure could be observed by SEM, indicating that these line structures were composed of deposited silver metal. The inset of Figure 2b showed that the wire structure consisted of silver nano-clusters. The AFM measurements of an electroless plated DNA-amphiphile polyion complex monolayer without cis-platin showed that only isolated dots were grown (data not shown). These dots were silver particles to which silver ions electrically adsorbed to the monolayer were reduced. The silver ions hardly adsorbed to the DNA because the phosphate group of the DNA molecule was blocked by both the substrate surface and the cationic amphiphile.

The platinum catalyst was essential for selective silver deposition along the matrix DNA molecule. Since Lambda DNA, which is a natural DNA extracted from a virus, has random base sequences, the reaction points of cis-platin in Lambda DNA is almost randomly arranged. Therefore the reduced platinum clusters were also aligned as shown in the inset of Figure 2a. The reaction of silver electroless plating can occur uniformly all over the stretched Lambda DNA molecules, following the scheme shown in Figure 1.

The conductivity of a single silver wire was investigated by conductive AFM (Figure 3c). The current between an Au-coated AFM tip and a small silver paste electrode placed on the surface through the wire structure were monitored under air as shown in Figure 3. In the current mapping, by applying 1 volt (Figure 3b), the brighter parts corresponded to higher electrically conductive

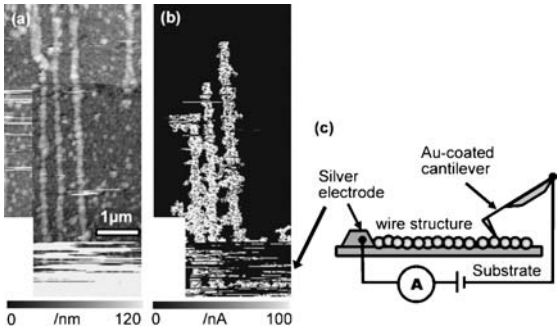

Figure 3. Conductive AFM images of wire-like structures: (a) Topographic image; (b) Electric current mapping image of (a). The diagram of conductive AFM is shown in (c).

parts between the fixed electrode and the AFM tip. Comparing with the topographic image (Figure 3a), the silver wire structure clearly had a very high conductivity over a length of ca. 6 μm. However, the wires were broken in the middle. These are due to defects such as an invisible grain boundary in the metal particles. The control of the joint between deposited silver nanoclusters is important to obtain straight breaking-free nanowires.

In conclusion, the fabrication of silver wire structures on template DNA molecules stretched and immobilized by the LB method has been achieved. Platinum clusters derived from cis-platin were not influenced on stretching the DNA molecules. The several μm length of conductive silver nanowires (<100-nm wide) could be prepared by homogeneous and selective silver deposition on the stretched DNA with the platinum catalyst. The DNA-based selective electroless plating method is a strong tool to fabricate nano-devices.

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