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DNA-Based Silver Nanowires Fabricated by Electroless Plating

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DNA-Based Silver Nanowires Fabricated by Electroless Plating

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The precise metallization of double-stranded DNA by the selective electroless plating method was investigated for the purpose of the fabrication of nanowires. Cis-platin was bound to template DNA molecules and reduced to platinum which can catalyze following silver metal deposition. The DNA molecules combined with the platinum clusters was stretched and immobilized on a glass substrate by using the LB method. The electroless plating of the platinum-bound DNA molecules immobilized on the substrate by reduction of silver ion gave uniform silver nanowires (ca. 30 nm height and 50 ~ 100 nm width) along the stretched DNA structures. On the contrary, the electroless plating of DNA molecules without the catalyst provided inhomogeneous silver deposition. Conductive AFM measurement revealed that the obtained silver nanowires as long as several μm had high conductivities.

Keywords: cis-platin; DNA; nanowire; polyion complex monolayer; selective electroless plating

INTRODUCTION

The fabrication of metal nanowires based on double-stranded DNA as template for metallization has attracted much attention from the view point of self-assembly manufacturing of custom-made nano-devices [1–5]. However, the number of experimental reports on conductivity

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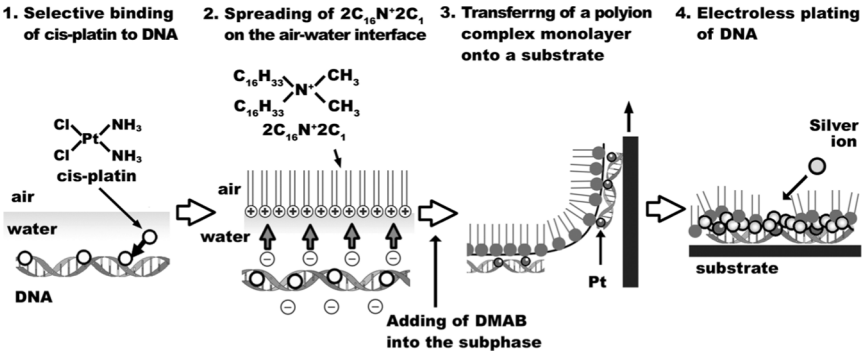

FIGURE 1 A scheme for the fabrication of silver nanowires by the selective electroless plating using stretched DNA as template.

measurements of DNA-based nanowires is very limited [5]. In this paper, we report the fabrication and the conductivity measurement of fine silver nanowires prepared from stretched DNA molecules by using a selective electroless plating method.

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 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 Langmuir-Blodgett (LB) method, DNA molecules were immobilized on the glass substrate in a stretched configuration [7]. The silver metal deposition of stretched platinum-bound DNA immobilized on the substrate was investigated.

EXPERIMENTAL

A DNA-amphiphile polyion complex monolayer was formed by spreading dihexadecyldimethyl ammonium bromide ($2C_{16}N^+2C_1$) (Sogo pharmaceutical Co., Ltd.) on a Tris-HCl buffer solution (pH7.8 at

20°C) of 1.0×10^{-8} M (in base pair) Lambda DNA, 2.5×10^{-6} M cis-platin and YOYO-1 (if necessary). After the reduction of cis-platin to platinum by the addition of 10 ml of 25 mM DMAB 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. A fluorescence microscope (E-600, Nikon) was used for fluorescence observations [8].

Silver metal deposition on DNA was carried out by immersing the glass substrate on which stretched DNA with platinum clusters was immobilized 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. Then the glass substrate was washed with pure water and dried by blowing of nitrogen gas. and observed using FE-SEM (S-5200, HITACHI) and AFM (SPA400/S3800, SII).

RESULTS AND DISCUSSION

The fluorescence image of the transferred polyion complex monolayer shows that DNA molecules were stretched parallel to a lifting direction, though cis-platin was reduced in the subphase (Fig. 2(a)).

The glass substrate on which stretched DNA with platinum reduced was immobilized was immersed into a silver electroless plating solution for silver metal deposition on DNA. The spattering-free SEM

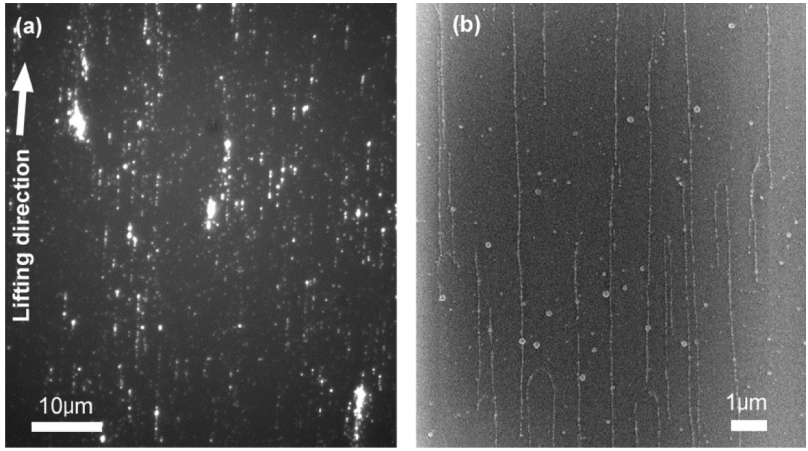

FIGURE 2 (a) The fluorescence image of a DNA-$2C_{16}N^{+}2C_1$ complex monolayer with reduced cis-platin. (b) The SEM image of a DNA-$2C_{16}N^{+}2C_1$ complex monolayer after silver electroless plating.

image of the silver-deposited surface was shown in Figure 2(b). 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 AFM measurements of an electroless plated DNA-amphiphile polyion complex monolayer indicated that the nanowires (ca. 30 nm height and 50 $\sim$ 100 nm width) were composed of silver clusters along the stretched DNA structures. The electroless plating of the DNA-amphiphile polyion complex monolayer without cis-platin showed that only isolated dots were grown (data is not shown here). This indicated that the platinum catalyst was essential for selective silver deposition along the matrix DNA molecule. Since DNA employed in this experiment has random base sequences, the reaction points of cis-platin in DNA are almost randomly arranged. Therefore the reduced platinum was also aligned on DNA. Therefore the reaction of silver electroless plating can occur uniformly all over the stretched DNA molecules, following the scheme shown in Figure 1.

The conductivity of a single silver wire was investigated using conductive AFM (Fig. 3(c)). In the current map measured by applying 1 Volt (Fig. 3(b)), the brighter parts corresponded to higher electrically conductive parts between a fixed electrode and an AFM tip. Both of the topographic image and the current map were turbulent due to contact-mode AFM measurement. Comparing with the topographic image (Fig. 3(a)), the current map clearly revealed that the silver nanowire had a very high conductivity. However, non-conductive parts were observed in the middle of the nanowires (the left side of Fig. 3(b)). Formed silver nanowires could be fragile. While the AFM tip scanned the surface from upward to downward in Figure 3, the AFM tip

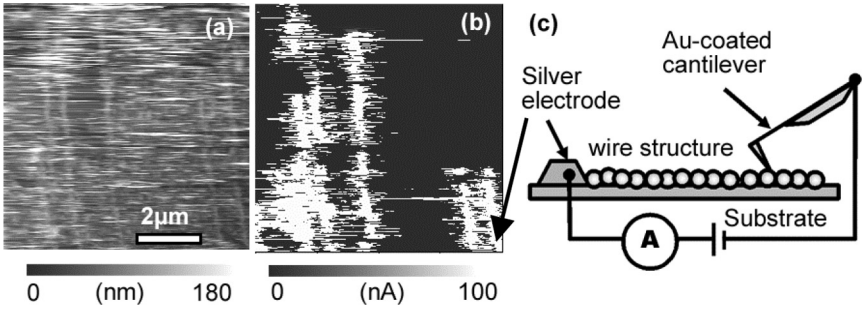

FIGURE 3 Conductive AFM images of wire-like structures: (a) Topographic image; (b) Electric current mapping image of (a). The diagram of conductive AFM is shown in (c).

removed the portions of the silver nanowires from the surface. Therefore the isolated conductive lines were observed. On the other hand the conductivities were not obtained whole at the nanowires (the right side of Fig. 3(b)). These were caused by defects such as an invisible grain boundary in the metal particles. The control of the joint between deposited silver nano-clusters is important to obtain straight breaking-free nanowires.

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