09:45 – 10:30

Enzymatic synthesis of a DNA triblock copolymer composed of natural and unnatural nucleotides for preparation of a nano-gap electrode

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Nucleobase-selective metallization of DNA has been expected to enable the fabrication of nanostructured electronic devices such as a nano-gap electrode and a p-n junction by self-organization. We showed that a DNA-templated gold nanoparticle (AuNP) / polyaniline-alternated hybrid nanowire, with a configuration resembling that of a one-dimensional array of tunnel junctions, could support Coulomb blockade transport [1]. The AuNPs act as the conductor, while the polyaniline serves as the capacitor junctions, with the two components alternately aligned on DNA in a sequential assembly process.

In order to prepare conductive nanowires with natural DNA, we employed guanine N_7-binding cis-platin as the precursor of catalyst for electroless plating of λ-DNA [2]. Cis-platin bound to λ-DNA was transformed to

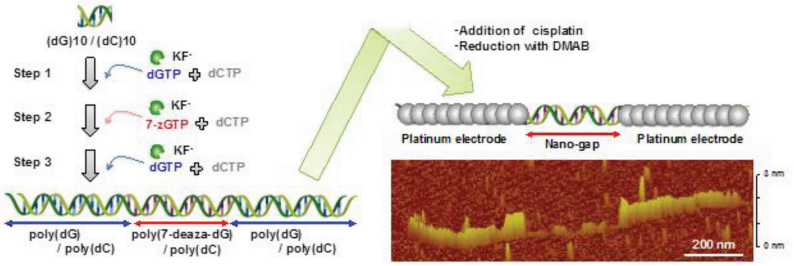

Figure 1 Fabrication of metal nanowires based on DNA-templated metallization of a DNA triblock copolymer

Pt cluster by chemical reduction. After stretching the Pt-deposited λ-DNA by LB method, rapid and selective deposition of Ag on DNA was achieved upon the introduction of Ag^+ and reducing agent. This biometallization approach provided linear Ag NWs of 50–100 nm in width with high conductivity [3]. To apply sequence specificity of DNA for metal deposition, we synthesized DNA diblock copolymer composed of poly(dG)-poly(dC) (GC part) and poly (dAT) (AT part) by using the Klenow fragment exo^- as the polymerase [4]. This artificial sequence thereby allows cis-platin to selectively interact with the GC segment, other than the AT part. The reduction of cis-platin further led to a sequence-specific Pt deposition on the stretched DNA. Construction of novel tunneling nanostructures via DNA templating was explored. Reduction of cisplatin bound to guanine (G) of DNA can provide Pt nanowires. Meanwhile, 7-deaza-G is expected not to be bound to cisplatin because N_7 which binds to cis platin is changed to C_7. In this report we synthesized DNA triblock copolymers consisted of poly(dG)-poly(dC) and poly(7-deaza-dG)-poly(dC) blocks by enzymatic reactions for the preparation of nano-gap electrodes by deposition of Pt onto the poly(dG)-poly(dC) block. It is expected that the poly(7-deaza-dG)-poly(dC) block part acts as a nano-gap (Figure 1).

For that purpose DNA homopolymers such as poly(dG)-poly(dC), poly(7-deaza-dG)-poly(dC) and triblock copolymer poly(dG)-poly(dC) / poly(7-deaza-dG)-poly(dC) / poly(dG)-poly(dC) were synthesized from dG_{10} and dC_{10} as template primers using DNA polymerase Klenow fragment exo^-. Molecular weight of synthesized DNA polymers was measured by electrophoresis. The DNA polymers were immobilized on mica substrates by the LB method and were reacted with cis platin and reduced. Heights of the DNA polymers were measured by AFM.

About 3,000 bp of poly(dG)-poly(dC) was obtained by 1 h of polymerization reaction in the presence of dGTP and dCTP. When 7-deaza-dGTP was added instead of dGTP, 3,000 bp poly(7-deaza-dG)-poly(dC) was obtained. Poly(7-deaza-dG)-poly(dC) could be polymerized in almost the same speed of poly(dG)-poly(dC). CD spectra and Tm measurement showed that the structure of poly(7-deaza-dG)-poly(dC) was much differ from that of poly(dG)-poly(dC). By changing of the dNTPs from dGTP to 7-deaza-dGTP, triblock copolymer DNA was synthesized. After reduction of cis platin the DNA block copolymer was observed by AFM. The image showed that height of one block increased due to the deposition of platinum metal, indicating that cis platin was selectively bound to guanine, not to 7-deaza-guanine in

this experimental condition. It is expected that reduction of cisplatin with the triblock copolymer can provide the nano-gap electrodes.

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