Translocation of Single Stranded DNA through Nano-Cylindrical PEO Passage Self-Assembled by Amphiphilic Block Copolymer

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Advances in solid-state nanopore sensors are positioning them as a promising technique for label-free DNA sequencing. One of the major issues still to be overcome is to reduce translocation speed of DNA molecules, so that the nucleotides can be distinguished in adjacent order with high accuracy. In this paper, we report a novel approach for slowing DNA translocation by applying a nano-cylinder occupied by hydrophilic polymer chains as a transport channel.

A block copolymer composed of polyethylene oxide (PEO) and poly(methacrylate) bearing azobenzene mesogens in their side-chains (PMA(Az)) was applied to self-assemble ordered array of hydrophilic PEO cylinders (diameter: 2 ~ 9 nm) in hydrophobic PMA(Az) matix.[1] Sensor chips were fabricated by coating the block copolymer thin film on SiN membrane with a pore (diameter: 30 ~ 50 nm) and assembling the PEO cylinders perpendicularly on the membrane (Figure 1). The limited number of PEO cylinders, which were aligned on the underneath pore served as translocation passages. The translocation of single stranded DNA (ss-DNA) fragments through the PEO cylinders was studied by following the standard method[2]. The sensor chip was set in between two flow cells and filled with buffer solution containing 1M KCl. Single stranded poly(deoxyadenylic acid) (ss-poly(dA)) was introduced into the *cis*-side of the cell and translocated through the sensor chip by applying trans-chip potential. The translocation events were clearly detected as blockades in the ionic current flowing through the PEO cylinders (Figure 2). The velocity of the ss-poly(dA) was statistically evaluated from the dwell time t_D of the blockade events and was measured to be in the range of 10 ~ 100 μsec/base (Figure 3), which was 1 to 2 orders slower than that achieved by conventional solid-state nanopore sensors.

As one end of the PEO chains filling the cylinders are fixed on the interface between the cylinders and the surrounding PMA(Az) matrix, swelling of the PEO chains caused by immersion in the electrolyte solution is suppressed. Although further studies are required to fully reveal the mechanism, we consider that observed slowing-down effect was caused by the interaction between DNA molecules with high-density PEO chains filling the nano-size cylinders.[3]

1. T. Yamamoto et al., *Adv. Funct. Mater*. **21**, 918 (2011)
2. R. Akahori et al., *Nanotechnology*. **25**, 275501 (2014)
3. We thank Prof. T. Iyoda of Tokyo Institute of Technology and Prof. M. Komura of Numazu National College of Technology for useful discussion and for providing block copolymers used in this study.

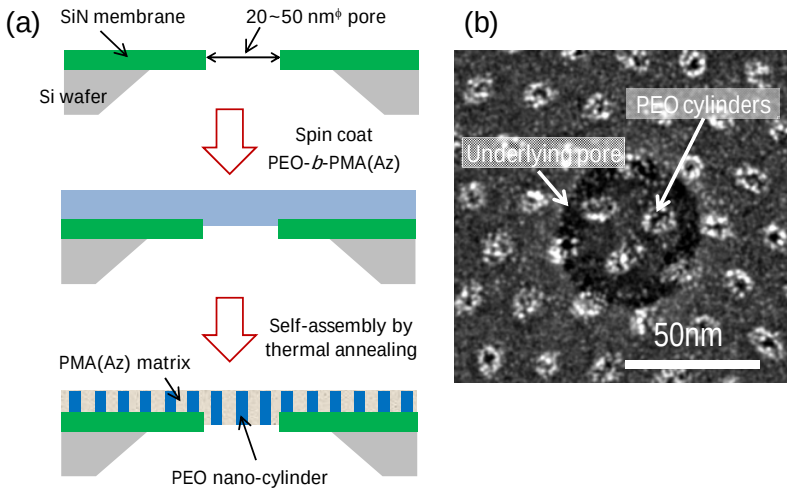

Figure 1 (a) Fabrication process and (b) scanning-transmission electron micrograph of the sensor chip. Diameter of PEO nano-cylinders: 9nm.

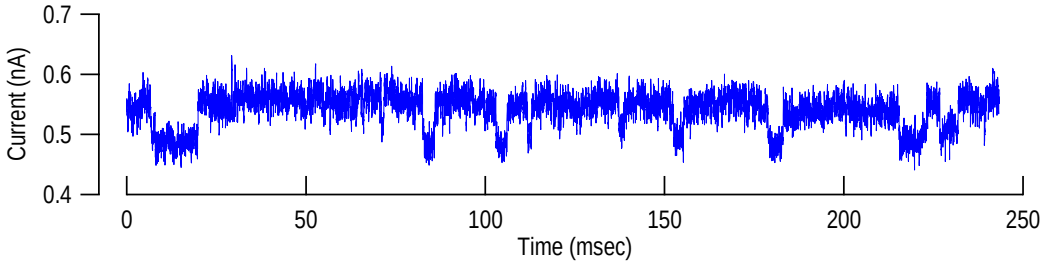

Figure 2 Profile of ionic current flowing though PEO nano-cylinders of the sensor chip. Blockades of ionic current caused by translocation of ss-DNAs were clearly detected. Sample: ss-poly(dA) 60mer. Diameter of PEO cylinder: 9nm.

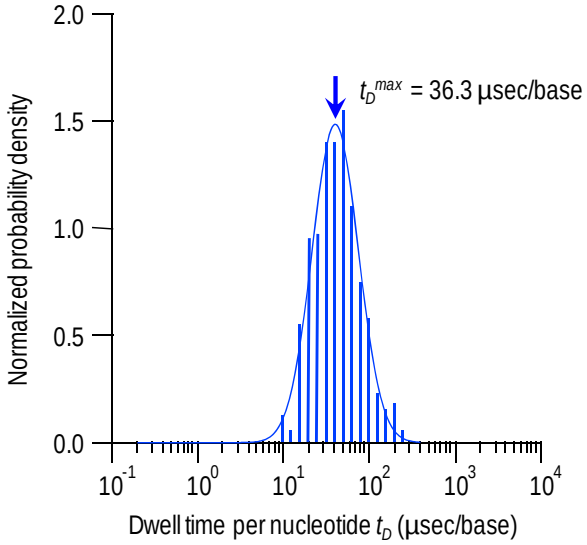

Figure 3 Dwell time histogram of ss-DNA translocation per nucleotide. Sample: ss-poly(dA) 60mer. Diameter of PEO cylinder: 9nm.