Chapter

Introductory Chapter: DNA as Nanowires

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1. Introduction

The integration of nanotechnology with biology and bioengineering has produced many advances with the manipulation of well-defined structures at the nanoscale with high accuracy. DNA molecules can be used for the assembly of devices, for the interconnect joints, or as the device element itself. Sequence-specific DNA detection has been applied in the diagnosis of pathogenic and genetic diseases. The unique physical properties of dots or wires with the remarkable recognition capabilities of DNA could lead to the miniaturization of biological electronics and optical devices, which includes the biosensors and probes. Numerous advantages of nano- and micro-biodevices include the separation technologies, HPLC and capillary electrophoretic separation of DNA, nanopillar devices for the ultra-fast separation of DNA and proteins, nanoball materials for the fast separation of wide range of DNA fragments and the nanowire devices for ultra-fast separation of DNA, RNA, and proteins. The studies about these devices have been carried out by *Prof. Yoshinobu Baba* and the research group [1–12]. The nanopillar, nanowall, nanoslit, and nanopore structures were designed by the top down or semiconductor nano-fabrication technology, while the nanoball, nanowire, nanoparticles and the quantum dot structures are designed by the use of bottom up or self-assembled nano-fabrication technology. These devices are shown in **Figure 1**.

DNA exhibits many other properties; as high stability, adjustable conductance, vast information storage, self-organising capability and programmability. So it is considered as an ideal material for the applications of nanodevices, nanoelectronics and molecular computing. There are several advantages to use DNA for these device designs. The first step of the DNA-based nanotechnology is to attach DNA molecules to the surfaces. It can be done by three different methods: by electrostatic interaction between DNA and a substrate, covalent binding of a chemical group attached to the DNA end and the binding of protein attached at the DNA end to the corresponding antibody immobilized at the surface. Seeman and co-workers [13] have exploited the properties of DNA's molecular recognition to design complex mesoscopic structures based solely on DNA. They used the branched DNA to form stick figures by properly choosing the sequence of the complementary strands. Further macrocycles, DNA quadrilateral, DNA knots, Holliday junctions, and other periodic crystal structures were also designed. DNA-mediated self-assembly of nanostructures has been extended to metallic nanowires [14–16]. In a study, DNA as a template was used to grow conducting silver nanowires [14]. The fabrication of gold and silver wires was used with the DNA as a template or skeleton [15]. Nguyen et al. developed an approach for the attachment of DNA to oxidatively open the ends of multiwall carbon nanotube arrays [17]. The carbon wall nanotubes can be used as electrodes to transmit electrical signals or as sensors to detect the concentration of chemical or

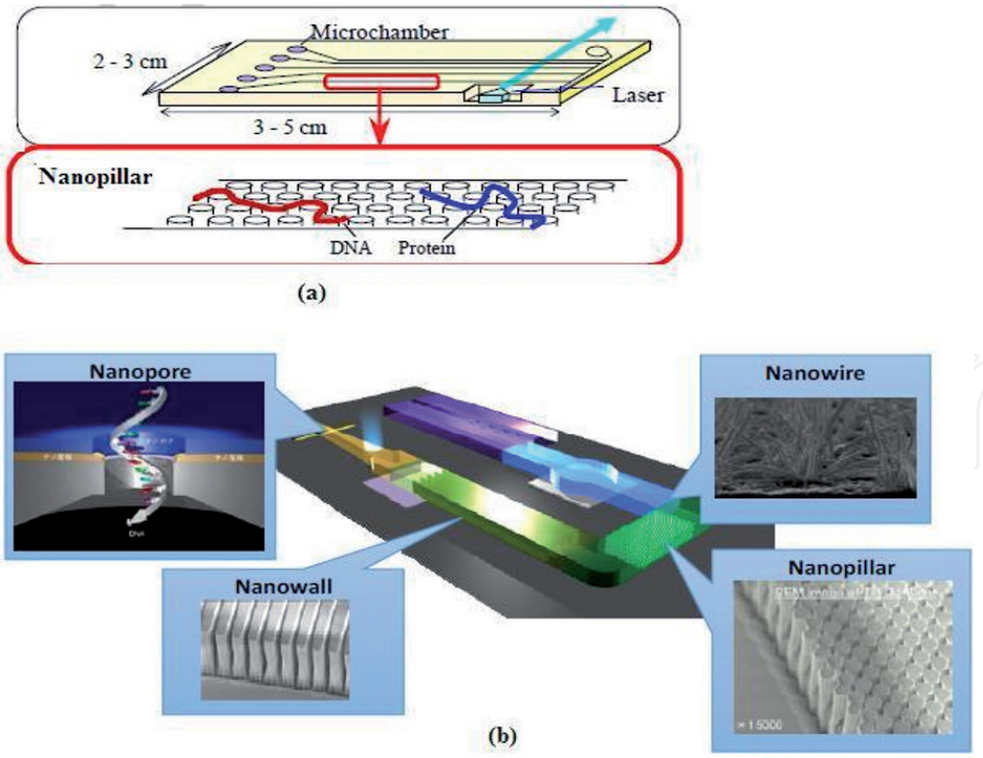

Figure 1.
(a) Device design of nanopillar and (b) nanobiodevices with nanopore, nanopillar, nanowire and nanowell. Adapted from Ref. [1].

biological materials [18–20]. Efficient DNA delivery is vital for the gene therapy, DNA vaccination and the advancement of other clinical therapies. Molecular devices are highly desirable as they can rapidly accumulate and displace electrons/charges within the nanoscale structures, and are sensitive to the changes in the physicochemical and biological environments. DNA logic gates can also constructed from the concepts based on the DNA tweezers [21]. Molecular wires and/or machines resemble electronic memory units can be made by cost-effective and low-energy technologies, so that they can provide the environmental friendly solutions. DNA origami has gained much attention recently because of its potential to direct the formation of predefined 2D or 3D DNA structures at the nanoscale [22].

DNA nanomachines can also be fuelled by enzymes or DNA [23, 24]. An enzyme-operated DNA-switch was proposed recently [24]. DNA-protein conjugates were widely applied in the development of immunoassays, biosensors, micro-chips and molecular devices [25]. A field effect transistor was also designed, based on the DNA base deoxyguanosine derivative [26]. The replacement of the natural bases can be carried out by the artificial nucleosides or nucleoside mimics [27]. Metal ions (Cu^{2+}, Pd^{2+}, and Ag^{+}) have been successfully incorporated as artificial DNA bases into the oligonucleotides [28]. Ni-DNA nanowires exhibit the characteristics of memristors, find potential application in mass information storage system [12]. The Ni-DNA device structure is given in **Figure 2**.

Assembling the biomolecules and microorganisms into a desired architecture has offered new routes to the fabrication of nanomaterials [29, 30]. DNA nanowires can be used as a template to fabricate functional nanomaterials and as a platform for genetic analysis [31–33]. These nanowires associate with an aqueous solution of DNA molecules, where capillary forces of the solution at a receding meniscus act to stretch and immobilize the molecules on a solid surface [34]. Yet

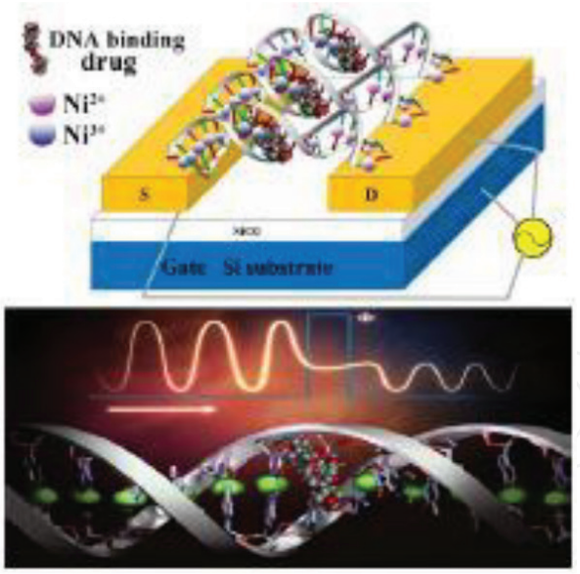

Figure 2.
Ni-DNA nanobiodevice structure. Adapted from Ref. [12].

the widespread use is still hindered due to the limited control over the size, geometry, and alignment of the nanowires. Hence to manipulate the size, geometry, and alignment of nanowires, efforts has been needed to control the evaporation of the solutions by adjusting the experimental parameters, such as: concentration and temperature, or by applying external forces that move the droplets in the desired direction [35–37].

2. Electrical characterization of DNA-based metallic nanowires

Novel conductive DNA-based nanomaterial, DNA-peptide wire composed of a DNA core and a peripheral peptide layer, is used for the wide variety of nano electronic and biosensor applications. The electrical conductivity of these wires is higher than the native double-stranded DNA (dsDNA). These wires produce high conductivity and better resistance to the mechanical deformations caused by the interactions between the substrate and electrode surface. Porath et al. [38] has studied the electrical transport through short (10 nm) dsDNA molecules deposited between platinum nanoelectrodes at different temperatures, confirming the reproducible semiconducting behavior with a gap [39, 40].

Electrical studies indicate that the charge transport in DNA is dominated by holes due to the position of the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) levels of DNA with respect to the Fermi energy of the coinage metal contacts (e.g., Au and Pt), though the photo physical studies indicate the transportation of both hole and electron in DNA [41]. As a result, DNA molecule behaves as a p-type nanowire [42]. The representation of conductive silver nanowires and nanoparticles NPs attached on the DNA origami are given in **Figure 3**.

The charge transport is explained by three main mechanisms: single-step-electron-tunnelling, thermal hopping, and domain hopping [43]. The charge transport in DNA occurs predominantly through the guanine bases due to their lowest electrochemical oxidation potential. When the DNA is absorbed on the surface, the conformations are affected by the van der Waals, electrostatic, and hydrophobic interactions within the substrate. Further the behaviour of DNA is

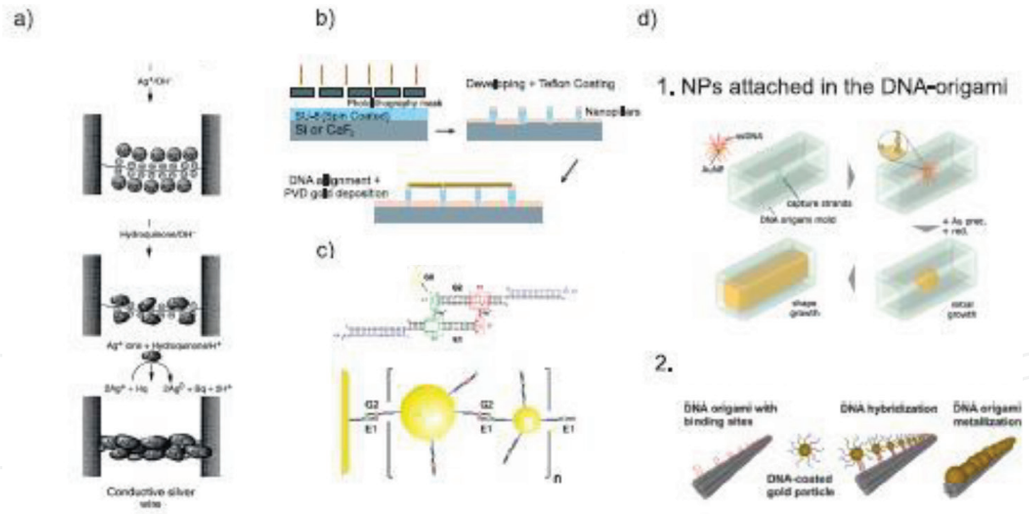

Figure 3.
(a) The construction of conductive silver nanowires, (b) PVD metal deposition on the alignment of DNA NW, (c) RNA functionalized AuNPs and (d) (1) DNA origami molds with Au nanoparticles and (2) nanoparticles NPs attached on the DNA origami. Adapted from Ref. [40].

affected by the DNA sequences, substrate and contact properties, temperature and humidity [44–46]. Recently, studies were conducted on the electrical measurements on guanine quadruplex DNA (G4-DNA), which is uniform in composition, consist of only G-nucleotides and it was observed that G4-DNA exhibit a greater bending rigidity compared to the dsDNA. Several techniques have been developed for contacting the nanowires with the combination of bottom-up and top-down strategies. These are:

a. Lithographically defined contacts and *in situ*/*ex situ* I–V measurements

b. Conductive AFM measurements

c. DNA Origami-based metal nanostructures

3. Conclusion

DNA acts as a promising material for biomolecular nanotechnology due to its unique recognition capabilities, physicochemical stability, mechanical rigidity and high precision processibility. Significant progress has been made in this field, but it is still in the early stages. The catalytic, electrical, magnetic, and electrochemical properties of such structures can be systematically investigated and will represent the new frontiers in this field. Various DNA-based nanostructures, including DNA itself, DNA functionalized with metal and semiconductor nanoparticles, DNA-directed nanowires, and DNA-functionalized carbon nanotubes are used in wider application for biological and medical applications. Due to the present applicability of DNA structures, these properties should be properly studied to provide an access to the new and useful electronic and photonic materials. The development of DNA nanowires has recently focussed its attention in three aspects: (1) customising the sequence of nucleic acids for better electrical conductivity with reduced mismatch pair complexes, (2) stacking targeted double-helical backbone for stable and rigid nanowires, and (3) interconnection of discrete DNA origami structures [47]. Though researches have been carried out for the achievement of these targets, the cost of experimental synthesis need to be address in near future.

Acknowledgements

RS acknowledges the financial assistance by the DST WOS-A (SR/WOS-A/CS-69/2018). RS is also thankful to her mentor Dr. Shrish Tiwari, Bioinformatics Department, CSIR—Centre for Cellular and Molecular Biology, Hyderabad for the support.

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