Relationship between the structure and electrical conductivity of 12-mer single-stranded polyadenine studied by scanning tunneling microscope†

H. Rozak,[*1,*2] W. N. Zaharim,[*2] I. Miyazaki,[*3] N. E. Ismail,[*2] S. N. Abu Bakar,[*2] D. Kernain,[*5] M. R. Samian,[*4] K. Ichimura,[*3] M. I. Mohamed-Ibrahim,[*2] S. Sulaiman,[*2] and I. Watanabe[*1,*2,*3]

DNA has received much attention over the past few decades owing to their unique feature of π-π stacking interaction between neighboring bases. This feature provides an effective medium for the electron transport process in DNA.[1] In biological phenomena, the electron transfer could be utilized to study the DNA damage and repair mechanism at the sub-atomic scale.[2]

How can we differentiate the characteristics of electron motion in normal and damaged DNA? Furthermore, will damage in DNA affect the electron hopping rate and mechanism of electron motion? In order to answer these questions, firstly, we need to clarify whether DNA bases (A, C, G, and T) are conductive. Once strong baseline data of electron transfer in each base have are accumulated, the data could be used as a reference for normal and damaged DNA. A lot of studies have been conducted in the past to investigate the electronic properties of DNA.[3] Their findings vary from insulating to semiconducting and metallic properties. In order to resolve this matter, two main techniques were used: scanning tunneling microscopy (STM) and muon spin relaxation spectroscopy (μSR). Measurements were performed 12-mer single-stranded (12-ss) adenine, cytosine, guanine, and thymine. But in this report, we only present the XRD and STM data of adenine (12-ssA).

XRD measurements were performed to characterize the structure of a 12-ssA molecules at room temperature, however, no sharp diffraction peaks were observed in the XRD pattern, which indicated that the 12-ssA sample is not crystallized and it is in an amorphous state as shown in Fig. 1.

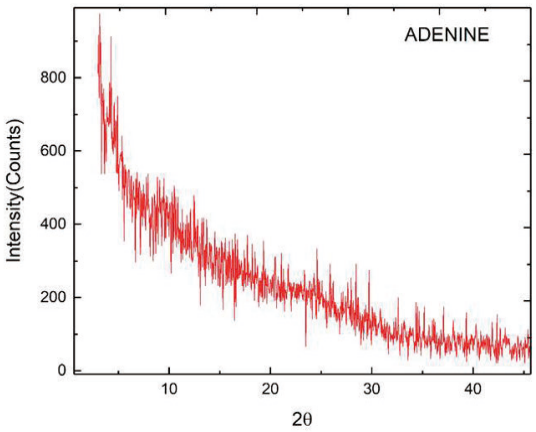

Fig. 1. XRD patterns of 12-ssA molecules measured at room temperature. The XRD patterns showed no sharp or enhanced diffraction peak, suggesting an amorphous state of the sample.

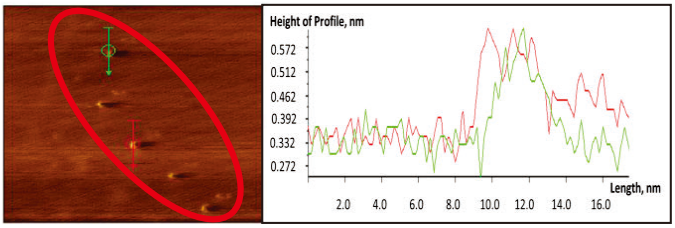

Fig. 2. The STM image of 12-ssA molecules that align in a one-dimensional chain structure and the analysis of the height profile of 12-ssA molecules.

For the STM measurements, the molecular structure of the 12-ssA molecule was probed to measure the height profile between the tip to the sample molecule (h). This height profile represents the efficiency of the electron tunneling from the tip to the sample, which could be related to the conductivity of the sample. The relation between the height profile (h) and the efficiency of the tunneling current (I) could be expressed as follows:

$$I = V \times \exp[-2\hbar^{-1}(2m\phi)^{1/2}h] \quad (1)$$

Where m is the electron rest mass and ϕ is the work function of the sample.[4] Based on Eq. (1), the current depends exponentially on the distance. If the distance between tip and sample surface increase, the tunneling current decreases.

In this study, the structure of 12-ssA molecules was found to be well observable on the graphite substrate as illustrated in Fig. 2. The structure of 12-ssA molecules was observed as bright spots in the red circle. The length of the molecule was about 4.3 ± 1.6 Å, and the side-by-side distance was 25 ± 7.5 Å. This figure indicates that 12-ssA was not perfectly insulating and had electrical conductivity because STM only probe the conductive sample.[5] The results of the height profile of 12-ssA molecules in Fig. 2 could be used to make a comparison with other samples (12-ssC, 12-ssG, and 12-ssT) in the future.

† Condensed from the article in Materials Science Forum. **966**, Trans Tech Publications Ltd., (2019)
*1 RIKEN Nishina Center
*2 School of Distance Education, Universiti Sains Malaysia
*3 Department of Engineering, Hokaido University
*4 School of Biological Sciences, Universiti Sains Malaysia
*5 Institute of Research in Molecular Medicine, Universiti Sains Malaysia

References

1) R. G. Endres *et al.*, Rev. Mod. Phys. **76**, 195 (2004).
2) M. A. Grodick *et al.*, Biochemistry. **54**, 962 (2015).
3) K. L Jiménez-Monroy *et al.*, J. Phys. Chem. A **121**, 1182 (2017).
4) T. Ohshiro *et al.*, Chem. Commun. **46**, 2581 (2010).
5) B. Bhushan, H. Fuchs, *Applied Scanning Probe Methods II.* (Springer-Verlag Berlin Heidelberg, 2006).