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A combined nonequilibrium Green's function/density-functional theory study of electrical conducting properties of artificial DNA duplexes

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ABSTRACT

DNA duplexes have attracted much attention as a primary candidate for nanowires possessing self-organizing capability. To employ DNA duplexes as nanowires, however, a major drawback must be overcome; the guanine bases undergo oxidative degradation in a hole transport through DNA duplexes, which is likely caused by the presence of adjoining adenine bases that do not effectively mediate the charge transport through DNA duplexes. To overcome the drawback, several artificial nucleobases based on adenine have been designed and tested, confirming that the artificial nucleobase-containing DNA duplexes do not suffer from such an oxidative damage and exhibit high efficiency in hole transport through the DNA duplexes. In the present study, we examine the electrical conducting properties of these artificial DNA duplexes by use of nonequilibrium Green's function and density-functional theory methods. The results explicate the origin of the experimentally observed high conductivity through the DNA duplexes containing the artificial DNA bases. We also put forth a computer-aided design of novel artificial DNA bases with low ionization energies, and examine the electrical conductivity of the DNA duplexes containing the designer nucleobases for potential use as highly conductive nanowires.

1. Introduction

In recent years, various types of nano-sized materials have been developed for use in nanoscale devices to bring about a significant downsizing of the devices, beyond that of the currently available silicon-based devices. DNA duplexes have attracted much attention as a primary candidate for the nanowires holding self-organizing capability [1,2] and electrical conductivity [3–6]. To develop the DNA nanowires for use in nano-sized devices, however, a major drawback must be overcome; the guanine bases undergo serious oxidative degradation during a hole transport through DNA duplexes, which is likely caused by the adjoining adenine bases that do not effectively mediate the charge transport through DNA duplexes. In order to alleviate the oxidative damage, Okamoto et al. [7] designed three types of artificial nucleobases (Fig. 1) derived from adenine base, and confirmed that these artificial bases do not suffer from the oxidative damage and exhibit highly efficient hole transport through DNA duplexes.

Benzodeaza-adenine (BDA) shown in Fig. 1b was synthesized by attaching a benzene ring to adenine base (Fig. 1a). BDA has a number of π-electrons and a large stacking area between the neighboring bases in DNA duplex. It is therefore expected that the charge transfer through the DNA duplex containing BDA is more facile than that through naturally occurring DNA duplexes. In addition, the oxidation potential of BDA was found to be lower than that of guanine base. Okamoto et al. [7] considered that the origin of the low oxidation potential is primarily due to the hydrophobic character of BDA. They also synthesized methoxy-substituted BDA (MDA) and naphthalene-fused BDA (NDA), the chemical structures of which are shown in Fig. 1c and d. MDA has low ionization energy, while NDA has larger stacking area between the neighboring bases in DNA duplex. The experimental study [7] on charge transfer though DNA duplexes including these artificial DNA bases indicated that the DNA duplex containing MDA has the highest efficiency in hole transport, and that hole can migrate more than 6 nm through the DNA duplex without oxidative decomposition. Therefore, it is expected that the DNA duplex containing these artificial bases may be used as a highly conductive DNA wire. However, electrical conducting properties of these artificial DNA duplexes have not been investigated, because the experimental measurement of electrical conductivity through DNA duplex usually requires a large-scale experimental instrument such as the scanning tunneling microscope.

Electrical conducting properties of various nanowires were investigated theoretically [8–16]. In particular, the conductivity in DNA duplex has been evaluated by various methods as overviewed in the review article [8]. The ab initio and molecular dynamics studies [9] for DNA duplexes in water examined the dependence of electron transport in DNA duplex on the DNA base

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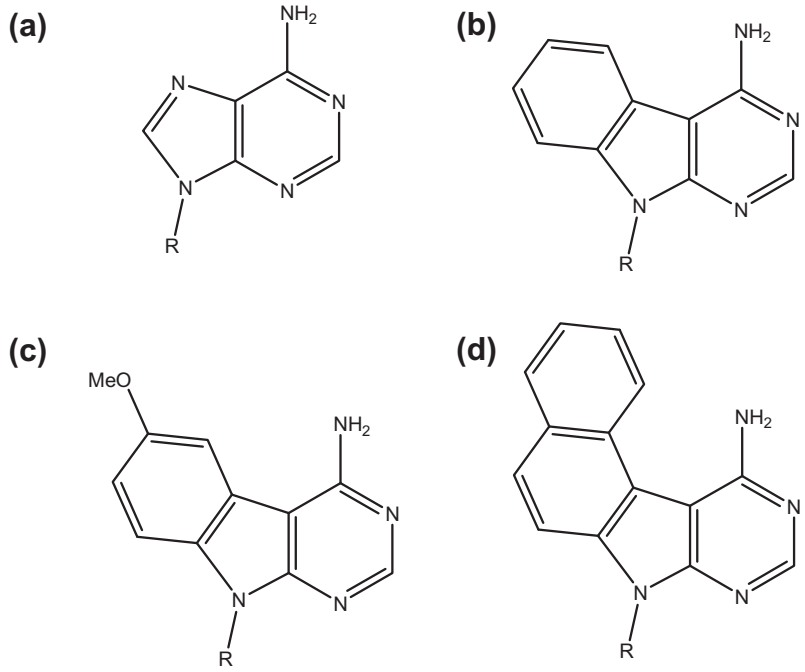

Fig. 1. Chemical structures of adenine and artificial bases synthesized by Okamoto et al. [7]: (a) adenine, (b) BDA (benzodeaza-adenine), (c) MDA (methoxy-substituted BDA) and (d) NDA (naphthalene-fused BDA).

sequence, while the energetics of the DNA basepair degrees of freedom and their effects on the overall charger transfer processes in DNA were investigated [10]. In addition, charge transport properties in polyyne-based molecular wires [11], conjugated aromatic molecular junctions [12], atomic carbon nanowires [13] and coupled quantum dots [14] were studied theoretically. The effects of external electric field [15] and electron–phonon coupling [16] on the conductance were also studied by using the Landauer's scattering formalism.

In the present study, we simulate the electrical conducting properties of the DNA duplexes containing the artificial nucleobases designed by Okamoto et al. [7] by means of a suite of programs [17] based on the nonequilibrium Green's function and density functional theory (DFT) [18,19] algorithms. The simulation conducted at the molecular level explicates the origin of the observed high conductivity through the DNA duplex containing the artificial nucleobases. To design in silico additional artificial nucleobases that exhibit high conductivity through DNA duplexes, we carry out a computer-aided design of novel artificial nucleobases with low ionization energies, and examine the electrical conductivity of the DNA duplexes containing these artificial nucleobases.

2. Methods of calculations

2.1. Structure optimization of DNA duplex composed of artificial bases

In order to obtain stable structures and electronic properties of the artificial DNA bases synthesized by Okamoto et al. [7] (Fig. 1), we first optimized their structures by use of the DFT program DMol^3 [20,21]. The revised PBE [22] functional was used for the exchange and correlation potentials, while the DNP basis set (double-numeric quality basis set augmented with polarization functions) [21] was used in the DFT calculations. The ionization energies for the artificial DNA bases were estimated from the highest occupied molecular orbital (HOMO) energy, based on Koopmans' theorem [23].

Since the experimental study [7] indicated that the contiguous sequence of artificial DNA bases is important for facile hole transport through the DNA duplexes, the initial structure of the artificial DNA duplex was constructed from the ideal B-form structure of the naturally occurring DNA duplex composed of four adenine–thymine base pairs and backbones. In this 5′-d(AAAA)$_2$-3′ duplex, the adenine bases were replaced by the artificial DNA bases, and the structures of the replaced parts were partially optimized by using the DFT program DMol^3 [20,21]. Subsequently, atomic charges of each atom in the artificial DNA duplexes were evaluated by the DFT calculation, and the resulting charges were used as the charge parameters in the classical molecular mechanics and molecular dynamics calculation program AMBER9 [24]. The structures of the artificial DNA duplexes were fully optimized in the vacuum by use of this program. In the AMBER9 optimization, the PARM99 force field was assigned for the artificial DNA duplexes, and the threshold value of the energy gradient for the convergence was set as 0.001 kcal/mol/Å.

2.2. Calculations of electronic states and electrical conducting properties of artificial DNA duplexes composed of experimentally synthesized DNA bases

To investigate electrical conductivity of each of the artificial DNA duplexes, two Au electrodes were each tethered to the terminal bases of the DNA duplexes as shown in Fig. 2. The structure of the Au electrode was modeled from the Au(1 1 1) surface, because DNA duplexes are attached to this surface in numerous experimental studies [6]. This model contains 44 Au atoms and consists of 2 units of a periodically repeated unit-cell of the Au crystal. It is thus possible to obtain the density of electronic states for a semi-infinite Au electrode by using the periodicity of this Au model. The surface of each of the Au electrodes is stacked in parallel to the terminal DNA base on its center of gravity. The configuration of the connection between DNA duplex and Au electrodes is nearly the same as that employed in a previous theoretical study by Tada et al. [25]. As