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Photocurrents in DNA

Relationship between Charge Transfer and Charge Recombination Determines Photocurrent Efficiency through DNA Films**

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Long-range charge transport through a DNA duplex is mediated by the π-stack array of nucleic acid base pairs.[1] The features of DNA as a highly organized scaffold and effective medium for long-range charge transfer would be suitable for constructing the functional supramolcular assembly that performs the electronic logic gate, information storage, and signal processing.[2,3] In principle, electron-transfer chemistry, which can be directly converted into electrochemical signals, is quite compatible with electrochemical techniques. An electrochemical DNA sensor constructed on a solid surface by using the principle of charge transfer along the DNA duplex has been developed for practical biological applications ranging from DNA sequencing to genetic-mutation detection and single-nucleotide polymorphism (SNP) analysis.[4–8]

Photoelectrochemical approaches provide several advantages compared with conventional electrochemical methods.[9,10] By using light as an external stimulus at an appropriate wavelength, a selective electrochemical reaction can be achieved. In addition, an electrochemical method that uses a photocurrent can operate at a low applied potential, offering the stability of DNA films, extremely low background current, high sensitivity, and repeating cycles.[11] Another important aspect of a photoelectrochemical device is the application in a light–energy conversion system, which mimics solar-energy conversion during natural photosynthesis.[12,13] Nevertheless, there are only a few reports concerning DNA-based photoelectrochemical devices.[14–16] In particular, a fundamental understanding of the photocurrent generation through DNA films has not been developed, which is essential for the further development of such a device. Herein, we describe how important the relative rates of charge recombination and charge transfer are for the efficient photocurrent generation through DNA films and show the effect of a single base mismatch on the photocurrent efficiency.

DNA-modified gold surfaces have been used for electrochemical study of the electron-transfer process through DNA,[5,17,18] and the structural features of DNA on the surface have been well characterized.[17,19,20] DNA-modified films were constructed by the hybridization of thiolated DNA immobilized on a Au surface with naphthalimide (NI)-labeled complementary DNA. NI was selected as the photosensitizer because the photophysical properties for NI were well characterized and it strongly associates with DNA by stacking interactions.[21] In addition, the kinetics of the charge-separation and charge-transfer process in NI-modified DNA was characterized by our group by using time-resolved transient absorption measurements.[22–24] Figure 1 a shows a schematic illustration of the photocurrent generation process along DNA films on a Au electrode by the excitation of a photosensitizer. In a previous study, we showed that the photosensitizer, which has a high-enough reduction potential to oxidize an adjacent A base, leads to the charge-separated state with a long lifetime through the cascade electron-hole hopping.[22] As NI in the singlet excited state ($^1NI^*$) has large reduction potential ($E_{red}(NI) = -1.0$ V versus a normal hydrogen electrode (NHE), $E_s(^1NI^*) = 3.4$ eV, $E_{red}(^1NI^*) = 2.4$ eV; E_s = singlet energy), the photoexcitation of NI provides the charge-separated state between NI and the neighboring A base (contacted ion pair: $NI^{\bullet-}$-$A^{\bullet+}$) in the picosecond timescale.[25] A hole on A base migrates to the G base

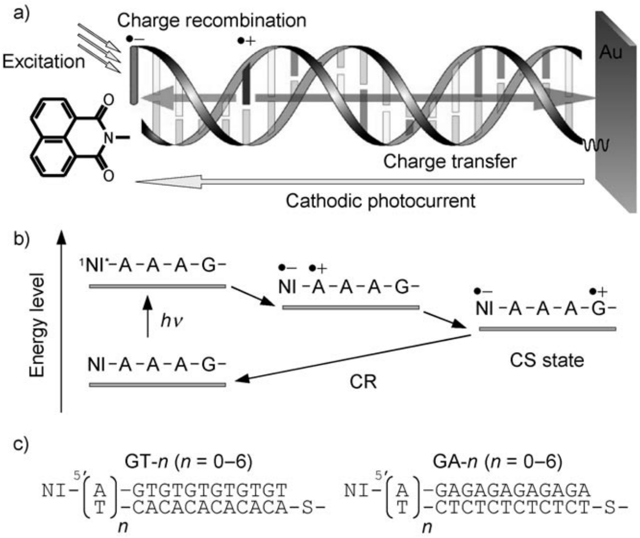

Figure 1. a) Schematic representation of cathodic photocurrent generation along the DNA duplex, which is immobilized on a gold electrode. b) Mechanistic scheme showing charge separation by hopping between A bases and leading to the formation of a charge-separated (CS) state and a charge-recombination (CR) process. c) DNA sequences used in this study. A photosensitizer, naphthalimide (NI), and thiol group are attached at both 5′-ends of the DNA.

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by hopping between A bases, leading to the charge-separated state between NI and G (Figure 1 b). The resulting positive-charge transfer by hopping between the G bases through DNA to the Au electrode and the electron removal from the reduced NI provide the cathodic photocurrent.[15,26,27]

In an effort to explore the relationship between the photocurrent generation and charge-transfer process, we designed two kinds of DNA molecules (GT-*n* and GA-*n*) in which NI and the nearest G base are separated by various numbers of A/T base pairs (*n*) (Figure 1 c). The GT-*n* and GA-*n* sequences have alternating GT or GA sequences as charge-conduction regions. The charge-recombination process between the photosensitizer (NI) and the hole-trapping site (G) can be modulated by changing the number of A/T base pairs. The positive-charge transfer rates through DNA after the formation of the charge-separated state can also be controlled by changing the sequence from the GT- to GA-repeat sequences.[28]

The cathodic photocurrent responses observed for the GT-*n* and GA-*n* series generated upon exposure to 365-nm light at -100 mV are shown in Figure 2. In GT-*n*, the photocurrent was not detected for $n = 0$–2, and a very weak photocurrent was observed for GT-3. At $n = 4$, the irradiation of the DNA films exhibited a quick response with high photocurrents, and the intensity slightly decreased with the increasing number of *n* up to 6. Almost similar results were observed in the GA series, but unlike GT-*n*, GA-3 showed high photocurrents. Figure 3 shows the plots of the photocurrent efficiency (I_{pc}) for GT-*n* and GA-*n* along with the charge-separation yields (Φ_{CS}), charge-recombination rates (k_{CR}), and charge-transfer rates (k_{CT}) for GT- and GA-repeat sequences derived from previous reports.[23,24] At $n = 3$, it should be noted that the charge-recombination rates are between the charge-transfer rates for GT-*n* and GA-*n*. In GA-3, the charge transfer ($k_{CT} = 5 \times 10^7\,s^{-1}$) is faster than the charge recombination ($k_{CR} = 3.3 \times 10^6\,s^{-1}$). As a result, the efficient photocurrent was observed for GA-3. In contrast, the charge transfer ($k_{CT} = 2 \times 10^6\,s^{-1}$) for GT-3 cannot compete with the charge recombination, resulting in very weak photocurrents. These results clearly demonstrate that the relationship between the charge transfer and charge recombination is critical for the photocurrent generation in DNA films. Once the charge recombination becomes slower than the charge transfer, the photocurrent intensity is determined by the charge injection yields ($n = 4$–6). Interestingly, as shown in Figure 2 d, the applied potential substantially promoted the photocurrent efficiency of GA-3 when compared with the other sequences. This shows that the acceleration of the charge transfer along DNA by the applied potentials on the surface improves the photocurrent efficiency.

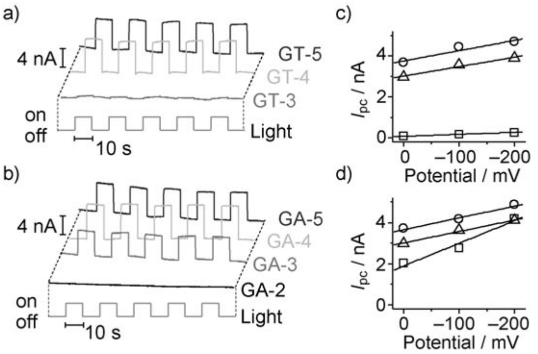

Figure 2. Photocurrent responses of DNA films at a potential of -100 mV upon UV illumination (365 nm) for a) GT-*n* ($n = 3$–5) and b) GA-*n* ($n = 2$–5). The dependence of photocurrents for c) GT-*n* and d) GA-*n* ($n = 3$: □, $n = 4$: ○, $n = 5$: △) upon an applied potential in the range from 0 to -200 mV. The potentials are measured versus Ag/AgCl (1 M KCl) reference electrodes. I_{pc} = photocurrent intensity.

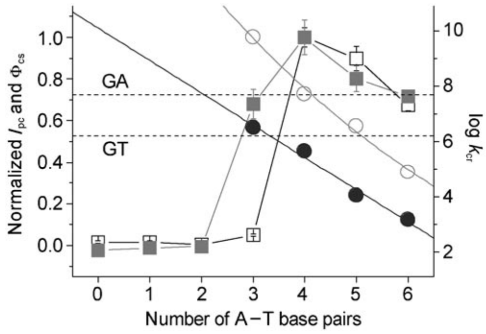

Figure 3. Relationship between I_{pc} for GT-*n* (□) and GA-*n* (■) at a potential of -100 mV and photochemical parameters, charge-injection yields (Φ_{CS}; ○), and charge-recombination rates (k_{CR}; ●). Photocurrent intensities for GT-*n* and GA-*n* are normalized at their maximum. The values of Φ_{CS} are normalized at $n = 3$. The dashed lines represent the charge-transfer rates for GT-*n* and GA-*n*. The values of Φ_{CS}, k_{CR}, and the charge-transfer rates for GT and GA sequence are derived from previous work.[22,24]

Energy diagrams of the photocurrent generation in the DNA films are shown in Figure 4. The photocurrent process is mainly divided into four processes, that is, charge injection, charge recombination, charge conduction along the DNA, and charge hopping to the Au electrode. The photocurrent generation efficiency is governed by the charge injection efficiency and the relationship between the charge conduction and charge recombination. The electron-hole flow generating photocurrents are gated when the charge conduction become

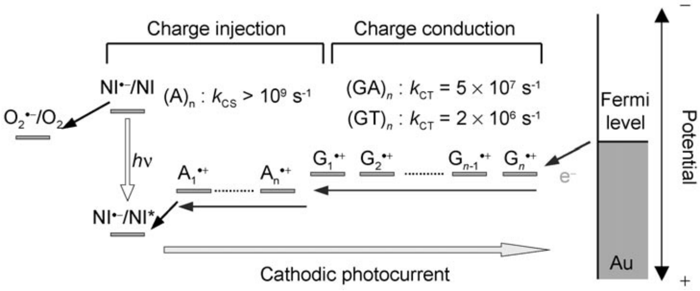

Figure 4. Mechanistic illustration of photocurrent generation in DNA films. DNA consists of charge-injection and charge-conduction regions. Cascade electron-hole flow from the Au electrode to NI along DNA provides the cathodic photocurrent. Charge-transfer rates for G hopping (k_{CT}) and A hopping (k_{CS}) are shown in the figure.

faster than the charge recombination. The applied potential on the electrode accelerating the charge transfer enhances the photocurrent when the charge conduction is competitive with the recombination process.

To evaluate the influence of the single-base mismatch on the photocurrent efficiency, we designed a DNA molecule containing an A/C mismatch in the charge-injection and charge-conduction region of both the GT-4 and GA-4 sequences. As shown in Figure 5, the photocurrent generation for GT-4-M1, GA-4-M1, and GA-4-M2 was strongly suppressed, whereas the A/C mismatch in the middle of GT-4 (GT-4-M2) showed a weak suppression,[29] meaning that the hole hopping between G bases across mismatch base pairs in GT-4-M2 was not retarded unlike the other sequences. The differences in the mismatch effect would reflect the local structural perturbation affecting the electronic interaction between nucleobases. These results clearly demonstrate that the mismatch effects on the photocurrent generation strongly depend on the position of the mismatch and the neighboring sequence that relates the charge-conduction rate.

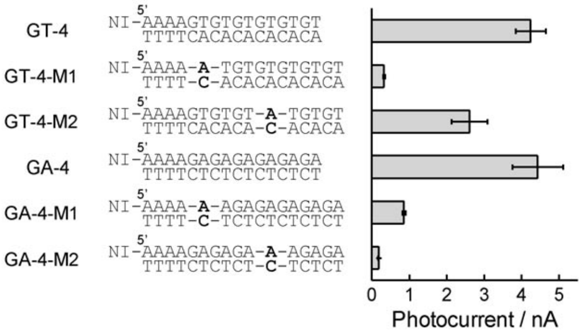

Figure 5. Photocurrent intensity obtained for matched and mismatched sequences. The mismatch sites are denoted by bold in the sequences.

In conclusion, we showed that the relationship between the charge transfer and recombination rates was essential for the photocurrent efficiency through DNA films on the Au electrode. We also found that the mismatch base pair incorporated in the sequence relating the charge-injection efficiency strongly inhibited the photocurrent generation. A mechanistic understanding of factors controlling the photocurrent generation in DNA films would contribute to the further development of DNA-based photoelectrochemical devices.

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[27] A low concentration of molecular oxygen (0.2 mM) does not affect the initial charge separation and recombination process as is indicated in Figure 1 b.
[28] Rate constants of the positive charge transfer (k_{CT}) for the GAG and GTG sequences are $4.8\times10^{7}\,s^{-1}$ and $1.6\times10^{6}\,s^{-1}$, respectively (see Ref. [22]).
[29] The surface density of the duplex DNA immobilized on the Au electrode were obtained by using the ruthenium(III) hexamine assay established by Tarlov's group. Significant differences in the surface density caused by different sequences and mismatch-containing sequences were not observed, indicating that the differences in the hybridization efficiency were not responsible for the mismatch effects (see the Supporting Information).