Photostimulated Hole Transport through a DNA Duplex Immobilized on a Gold Electrode

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Molecular engineering of artificial self-assemblies with desired functions on a surface has attracted much interest as an advancement of nanotechnology.[1] Self-assembled monolayers are good candidates for a stable and effective photoelectrochemical device for light-initiated electron transfer.[2] In recent years, DNA has also attracted much attention as a hole-transporting biopolymer,[3] and a number of studies on the electrochemistry of DNA-modified surfaces have been reported.[4] However, to our knowledge, there is no precedent in which a photocurrent is generated via long-range hole transport through a DNA monolayer on a solid surface from photostimulation. We assumed that the construction of well-organized hole-transporting DNA assemblies on a solid surface would produce a photocurrent arising from photostimulated hole transport through DNA.

Here, we report for the first time on the photostimulated hole transport through DNA duplexes immobilized on gold electrodes. By modifying the surface of a gold electrode with a DNA duplex containing a photosensitizer, such as anthraquinone, we have accomplished a DNA assembly that can induce a sequence-selective cathodic photocurrent, as illustrated in Figure 1.
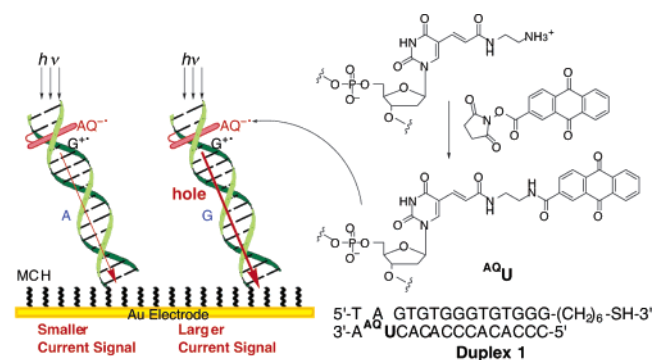

Figure 1. Schematic illustration of the measurement of a photocurrent using a gold electrode modified with an anthraquinone-modified DNA duplex (**Duplex 1**).

As shown in Figure 1, a thiolated DNA strand and a photosensitizer-labeled complementary strand were prepared. The photosensitizer-labeled strand was synthesized via postsynthetic modification of an amino-substituted DNA with the succinimidyl ester of anthraquinonecarboxylic acid. Anthraquinone has often been used as a photosensitizer[3c,5] as well as an effective redox-active material for electroanalytical chemistry.[6] Subsequently, mixed monolayer surfaces containing a thiolated DNA and 6-mercapto-1-hexanol (MCH) were prepared by immersing a gold electrode (2 mm² in area) in a 10 μM solution of a thiolated DNA, followed by exposure of the gold surface to an aqueous solution of 1 mM MCH to
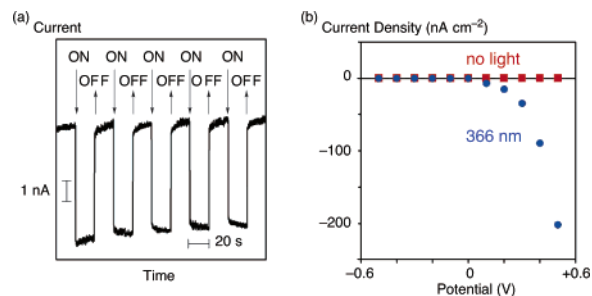
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Figure 2. (a) Photoelectrochemical response of the **Duplex 1**-modified gold electrode irradiated with 365 ± 5 nm light at 13.0 ± 0.3 mW cm⁻² with a 500 mV bias versus SCE. (b) Photocurrent versus applied potential curves for the **Duplex 1**-modified gold electrode irradiated with 365 ± 5 nm light at 13.0 ± 0.3 mW cm⁻² (blue circles) and nonirradiated (red squares). The bias on the electrode was changed from −500 to 500 mV versus SCE.
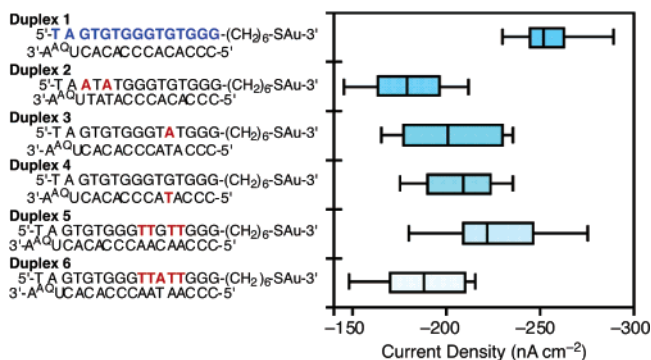

Figure 3. Photocurrent densities of different duplexes under 500 mV bias voltage. The duplexes in 10 mM sodium cacodylate (pH = 7.0) were irradiated (365 ± 5 nm light at 13.0 ± 0.3 mW cm⁻²) at 25 °C. Twenty experimental results obtained using different gold electrodes ((5.99 ± 0.52) × 10¹² DNA cm⁻²) are plotted for each duplex.[9]

minimize any nonspecific adsorption of the thiolated DNA.[7] By hybridization with the anthraquinone-labeled complementary DNA, the DNA duplex (**Duplex 1**)[8] was assembled on the surface of the gold electrode ((5.99 ± 0.52) × 10¹² DNA cm⁻²).

Photoelectrochemical measurements on the **Duplex 1**-modified gold electrode were carried out in a 10 mM sodium cacodylate (pH = 7.0) solution using 365 ± 5 nm light at a power density of 13.0 ± 0.3 mW cm⁻² in an applied potential of 500 mV versus SCE. Using an excitation wavelength of 365 ± 5 nm, only the anthraquinone was excited (ϵ_{365} = 4400). A stable cathodic photocurrent appeared immediately upon irradiation of the modified gold electrode (Figure 2a). We obtained a current density of −255 ± 15 nA cm⁻² for the **Duplex 1**-modified electrode (Figure 3). In contrast, the photocurrent dropped instantly when the illumination

ceased. These results indicate that the anthraquinone was the molecule responsible for the generation of the photocurrent.

The cathodic photocurrent increased sharply with increasing positive bias on the gold electrode, as shown in Figure 2b. The intensity of the photocurrent dramatically increased for increases in potential >0 V. This indicates that the photocurrent generation was controlled by a positive charge transport, i.e., hole transport between the gold electrode and the DNA. The dark current on the gold electrode remained near constant within the applied potential range, suggesting that the photocurrent flows to the gold electrode via the photoexcitation of anthraquinone.

It is well-known that oxygen acts as an electron acceptor in related photoelectrochemical systems. The semiquinone radical anion of anthraquinone is oxidized on reacting with dissolved oxygen.[5,6a-d] The concentration of dissolved oxygen in our solution was measured to be 8.3 ± 0.3 mg L^{-1} before bubbling argon through the solution. After bubbling argon through the solution, the concentration of dissolved oxygen decreased to 1.0 ± 0.2 mg L^{-1}, and the observed photocurrent in the **Duplex 1**-modified electrode decreased to -195 ± 25 nA cm^{-2}. This result indicates that oxygen acts as an effective electron carrier from the reduced anthraquinone in the present system and leads to higher current densities.

The efficiency of photostimulated hole transport through the DNA duplexes on the gold electrodes was strongly affected by the duplex sequences (Figure 3). The current densities of the electrodes modified by different duplexes were obtained by light excitation ($\lambda = 365 \pm 5$ nm) at a power density of 13.0 ± 0.3 mW cm^{-2} under a 500 mV bias voltage. When guanine (G), which acts as an effective electron donor in anthraquinone-photoinduced charge separation, was replaced by adenine (A) (**Duplex 2**), then the observed photocurrent was -175 ± 20 nA cm^{-2}, indicating the involvement of an efficient charge separation occurring between anthraquinone and G for photocurrent generation. In the hole transport mechanism, the bridged sequence taking part in the G-hopping strongly influences the hole transport efficiency.[10] Thus, we examined the photocurrent of a sequence where a G base, bridging the gap between two GGG units, was changed to an A base (**Duplex 3**). The photocurrent of the **Duplex 3**-modified electrode was -200 ± 25 nA cm^{-2}, and the decrease in current density shows that a G base is necessary for efficient hole transport on the gold surface. Next, we replaced the anthraquinone-labeled complementary strand of **Duplex 1** with the strand used in **Duplex 3** (**Duplex 4**). **Duplex 4** contained a G/T mismatched base pair. The observed photocurrent of a **Duplex 4**-modified electrode was -205 ± 20 nA cm^{-2}, indicating that the hole transport was suppressed. The disruption of the π-stacking array by the G/T mismatch strongly influenced the photocurrent intensity,[11] i.e., the photocurrent intensity was regulated by the replacement of the complementary strand.

In addition, we designed a sequence that contained a longer spacer unit (**Duplex 5**) and observed the resulting photocurrent. In hole transport through DNA, the length of the spacer sequences strongly influences the hole transport efficiency.[3d,10b] The observed photocurrent of a **Duplex 5**-modified electrode was -225 ± 20 nA cm^{-2}, which was lower than that observed for the **Duplex 1**-modified electrode. This result suggests that the hole transport efficiency was lowered by elongating the hole-hopping distance. The photocurrent was also examined for a duplex where the G base

of the bridge sequence in **Duplex 5** was replaced by an A base (**Duplex 6**). The observed photocurrent was -185 ± 20 nA cm^{-2}, and the hole transport efficiency was markedly suppressed. The photocurrent intensities observed in the series of experiments were sequence-selective, and the DNA was able to produce a high cathodic photocurrent when an appropriate sequence was selected.

In conclusion, photostimulated hole transport through DNA duplexes immobilized on gold electrodes has been investigated. By modifying a gold electrode with a DNA duplex containing a photosensitizer, we have observed a sequence-dependent cathodic photocurrent. Thus, DNA can serve as a good mediator for a cathodic photocurrent when an appropriate sequence is selected. Photoinitiated hole-transporting DNA molecules immobilized on a solid surface will facilitate the development of a variety of nanobiotechnological applications, from biosensors to photosynthetic model systems.

Supporting Information Available: Detailed experimental data on the synthesis and photoelectrochemical assays of the related DNA samples (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) Length of the duplex region of **Duplex 1** is ca. 4.6 nm.

(9) For a mixed monolayer surface containing 5′-AQU−(CH₂)₆−SH-3′ and MCH, a photocurrent density of -185 ± 15 nA cm^{-2} was observed.

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