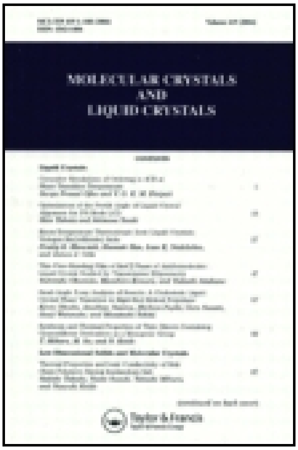

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"OR" LOGIC FUNCTION OF MOLECULAR PHOTODIODE CONSISTING OF GFP/VIOLOGEN/ CYTOCHROME *C* HETERO-FILM

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Molecular logic gate device with "OR" logic function was developed. The "OR" function logic gate was fabricated by the double line structured bio-photodiode, depicted as A and B line, consisted of Green fluorescent protein/viologen/ cytochrome c hetero-LB film. When a light was irradiated to a single (A or B) or double (A and B) line bio-photodiode as an input, the steady state photocurrent was generated in part of (A+B) as an output. The photocurrent intensity generated in one line input was lower than that of twin line input. The high photocurrent intensity indicates "1,1" in truth tables and low photocurrent indicates "0,1" or "1,0". Finally, "0,0" input corresponds to a dark state without light generation. The "OR" logic gate function was successfully achieved based on high- and low-photocurrent by threshold.

Keywords: green fluorescent protein; logic gate; molecular photodiode; OR logic function; transient photocurrent

INTRODUCTION

In the initial process of photosynthesis, a biological electron transfer system, photoelectric conversion occurs and then long-range electron transfer takes place very efficiently in one direction through the biomolecules [1–2]. The specific energy and electron transfer take place on a molecular scale due to the redox potential difference as well as the electron transfer property of functional molecules, especially the electron acceptors (A), sensitizer (S), and electron donor (D) [3].

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The concept or idea in the development of new functional bioelectronic devices can be inspired from the biological systems such as electron transfer chain or photosynthetic reaction center. By mimicking the organization of the functional molecules in the biological electron transfer system, the artificial bioelectronic device can be realized.

Various artificial biomolecular photodiode have been fabricated by mimicking the electron transport function of biological photosynthesis. Fujihira *et al.* reported the electrochemical photodiode using Langmuir-Blodgett (LB) films of three functional molecules or an aligned triad on the electrode, which worked in electrolyte solution [4,5] The optical and electrical characteristics of the molecular device consisting of flavin/porphyrin- or flavin/cytochrome c- hetero-LB films have been investigated [6,7]. The molecular photodiode consisting of hetero-organic LB film of four functional organic molecules, ferrocene, flavin, viologen, and TCNQ to be used as the electron donor, sensitizer, electron relay and electron acceptor units, respectively, were fabricated and photoinduced electron transfer was investigated. The authors reported that the fabrication of molecular photodiode consisting of Green fluorescent protein(GFP), viologen, and TCNQ was done and the photoinduced electron transfer of the device was observed [8,9]. However, the "OR" logic function of molecular-scale bio-logic gate device composed of electron transfer protein to be used as a molecular device has not been reported yet.

In this study the molecular bio-logic gate with "OR" logic function was investigated by using the bio-molecule based photodiode. For the logic function generation, molecular photodiode was arrayed with twin line structure. While the laser light is irradiated to the photodiode, the generated photocurrent was classified by threshold into high and low current. In order to investigate the photocurrent generation and to prove the logic function, steady state photocurrent was measured and analyzed.

EXPERIMENTAL DETAILS

Red shifted green fluorescence protein (rsEGFP), N-allyl-N′-[3-propylamido-N″,N″-di(n- octadecyl)]-4,4′-bipyridium dibromide (viologen), and Cytochrome c type IV from horse heart were used as an electron sensitizer (S), a first electron acceptor (A_1), and a second electron acceptor (A_2), respectively. The viologen was synthesized based on the previous experiments [9]. The GFP and cytochrome *c* were purchased from CLONTECH Co. and Sigma Chemical Co, respectively.

Using GFP (S, electron sensitizer), viologen (A_1, first electron acceptor), and Cytochrome *c* (A_2, second electron acceptor), the hetero-type LB film was fabricated onto the ITO coated glass. The deposition of LB films was carried out using a circular type Langmuir trough (Type 2011, Nima Tech., UK). Langmuir monolayers of A_1 and A_2 were compressed to a surface pressure of 37 mN/m and 25 mN/m, respectively, which were previously determined as target pressures for the optimal deposition of each material. 4 layers of A_1 and 1 layer of A_2 were then sequentially deposited onto the pretreated ITO substrate. For the LB film fabrication, Cytochrome *c* was dissolved in phosphate buffer solution of pH 8.0. For spreading the cytochrome *c* solution (4.0 mM) onto the subphase, cytochrome *c* solution was diluted with absolute ethanol and deionized distilled water (DDW). The volume ratio of ethanol, cytochrome *c* solution, and DDW was 2:2:1. The temperature was constantly maintained at 297 K [10].

The self-assembly (SA) technique was used to form the S layer on the A_1/A_2hetero-LB layers due to their high densities, without experiencing a loss of activity. S and A_1 interact and easily self-assemble due to electrostatic forces, since S molecules have a negatively charged surface at pH 8.0, due to its isoelectric point (pI) of 5.0 and A_1 has a positively charged head group at pH 8.0. Thus S can be easily and spontaneously adsorbed onto the surface of the A_1 layer. After S monolayers adsorption, the $S/A_1/A_2$ hetero-LB film was dried in a nitrogen atmosphere at 50°C [4].

To fabricate the metal/insulator/metal (MIM) structured device, the aluminum was deposited onto the hetero-film surface. For the logic function generation, double line structured molecular photodiode was constructed as shown in Figure 1. The size and separation length of each photodiode is 12×2 mm and 3 mm, respectively. To confirm the GFP adsorption surface morphology observation was done by atomic force microscopy (AFM, AutoProbe CP, PSIA, USA).

Laser light is irradiated on top of the single line- or double line-biophotodiode, and the generated photocurrent was summed. Then the photocurrent intensities of single and double line were easily distinguished from one another by threshold value. To distinguished the current difference in AND logic gate, In order to investigate the photocurrent generation and to prove the logic function, steady state photocurrents were measured and analyzed.

Figure 2 shows a schematic diagram of the experimental system for the photocurrent measurements. The light pulse from the laser system consisting of a N2 gas laser (6mW, 400mj, VSL-337ND, LSI, USA) was introduced to excite the GFP molecules. Pulse width and frequency were 10 ns and 200 MHz, respectively. With fast electronics using a 300 MHz frequency V/V amplifier (Model SR 240, Stanford research) and a storage oscilloscope of 500 MHz frequency (HP54616B, Hewlett-Packard, USA), the interlayer photocarrier movement was detected from a 50 Ω strip line geometry in order to acquire signals with high time resolution.

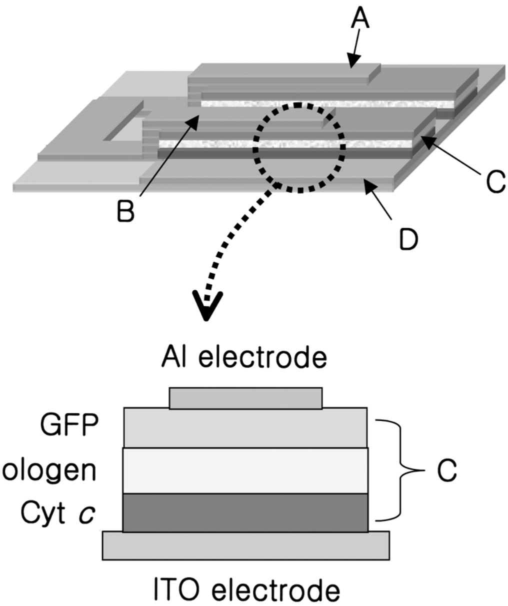

FIGURE 1 The schematic structure of “OR” function molecular bio-logic gate: A, B; aluminum top electrode, C; molecular hetero film, D; ITO electrode.

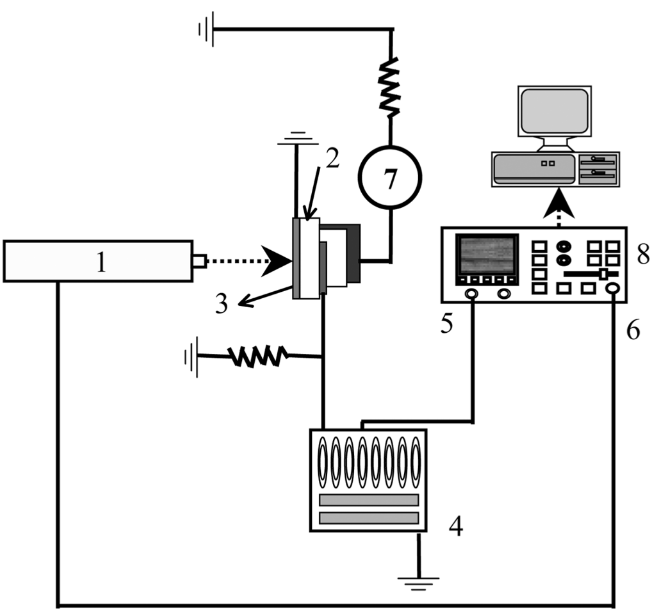

FIGURE 2 The schematic of the experimental system for the photocurrent measurements: 1; N_2 gas laser, 2; sample device, 3; Cu plate, 4; preamp SR240, 5; signal input, 6; trigger input, 7; external bias, 8; Oscilloscope HP 54610B.

RESULTS AND DISCUSSION

AFM analysis was performed to confirm the S adsorption in the proposed molecular hetero-film. AFM image of the S adsorbed A_1/A_2 hetero-LB is shown in Figure 3. In Figure 3, the S molecules were uniformly adsorbed onto the A_1 surface using electrostatic interaction. As shown in AFM image, the spherical type of aggregations of S molecules was observed, which indicated that the S molecules were partially adsorbed onto the A_1 surface. It is intimated that the S molecules were aggregated on the A_1 surface. The aggregation size of S molecules on A_1 surface was about $0.1 \sim 0.2\,\mu m$.

In the $S/A_1/A_2$ structured hetero-LB film, S is excited with light illumination ($S^*/A_1/A_2$). Excited electrons are separated ($S^+/A_1^-/A_2$) and transferred ($S^+/A_1/A_2^-$) to A_2 molecule via their redox potential difference [9]. Therefore unidirectional flow of electrons from S to A_2 can be occurred. The excited electrons are then separated and transported through the LB film. The dynamic process of electron transport can be observed based on the transient photocurrent. In the $S/A_1/A_2$ structured hetero-LB film,

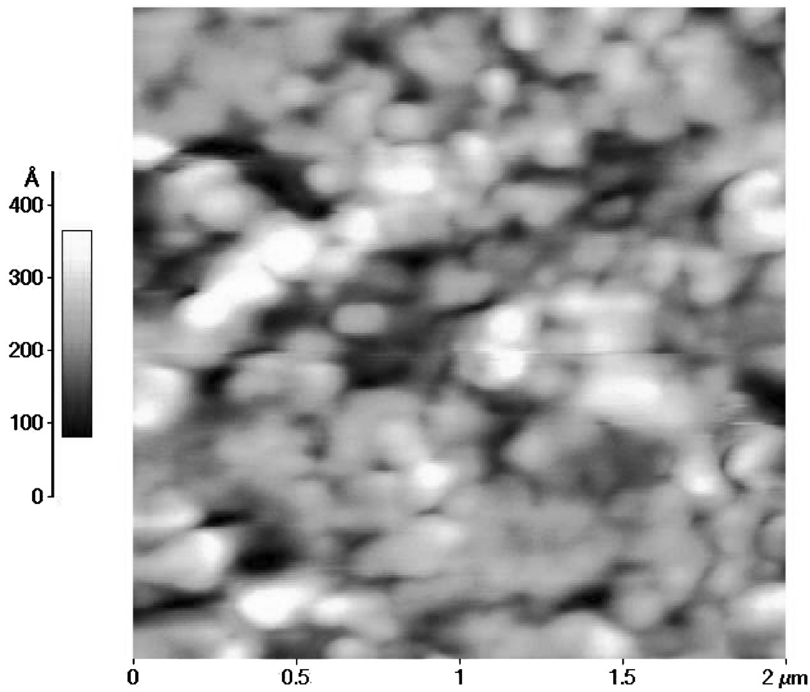

FIGURE 3 AFM morphology of GFP adsorbed layer.

photocurrent intensity is affected by the LB film thickness and summation of photocurrent. In the bio-logic gate device, logic function is investigated based on the transient-photocurrent intensity of device.

The proposed bio-logic gate device was read by monitoring photocurrent intensity at light irradiation. In the bio-logic gate, the low photocurrent intensity in single input irradiation indicates logically "0,1" or "1,0" in truth tables. In other hands, the high photocurrent generated in twin input irradiation indicates "1,1" in truth tables. Table 1 shows the logic factor and truth levels corresponds to light inputs. Laser light is irradiated onto the molecular bio-logic gate in part A and/or B. If light is irradiated onto the A or B (1,0 or 0,1), intensity and decay time of generated photocurrent of the bio-logic gate device are nearly the same. However, light is irradiated onto A and B (1,1), photocurrent intensity is twice as much as A(1,0) or B(0,1). Since "0,0" input was corresponded to the dark state without light generation, and the photocurrent caused by "0,0" input was not observed. Thus, the differentiation of photocurrent intensities in the proposed molecular bio-logic gate could be obtained. If the threshold as average point of photocurrent intensities is used, the logic function could be clearly separated from one another. However, it is difficult to distinguish the difference between "AND" and "OR" logic gate by threshold. To distinguish the current difference in "AND" and "OR" logic gate, external bias was applied between Al and ITO electrode. In "AND" logic gate, there are no external bias. In "OR" logic gate, 0.5 V bias was applied between Al and ITO electrode. The photocurrents of "OR" logic gate are higher than "AND" logic gate due to the external bias. In "AND" logic gate, the current at "1,1" is higher than the threshold 3 mV, and the current at "0,1","1,0" are lower than the 3 mV. Thus, the "AND" and "OR" logic gates are efficiently classified by the threshold 3 mV.

Figure 4(a) shows the experimental photocurrent results of molecular bio-logic gate with "OR" function. In this logic function, the pattern of photocurrent decay of "1,1" is similar with that of "1,0" or "0,1" but the intensity of "1,1" is clearly different from that of "1,0", "0,1". Photocurrent

TABLE 1 The "OR" Logic Factor and Truth Levels Corresponds to Light Inputs

A	B	Logic factor	Truth level
0	0	0	F
1	0	1	T
0	1	1	T
1	1	1	T

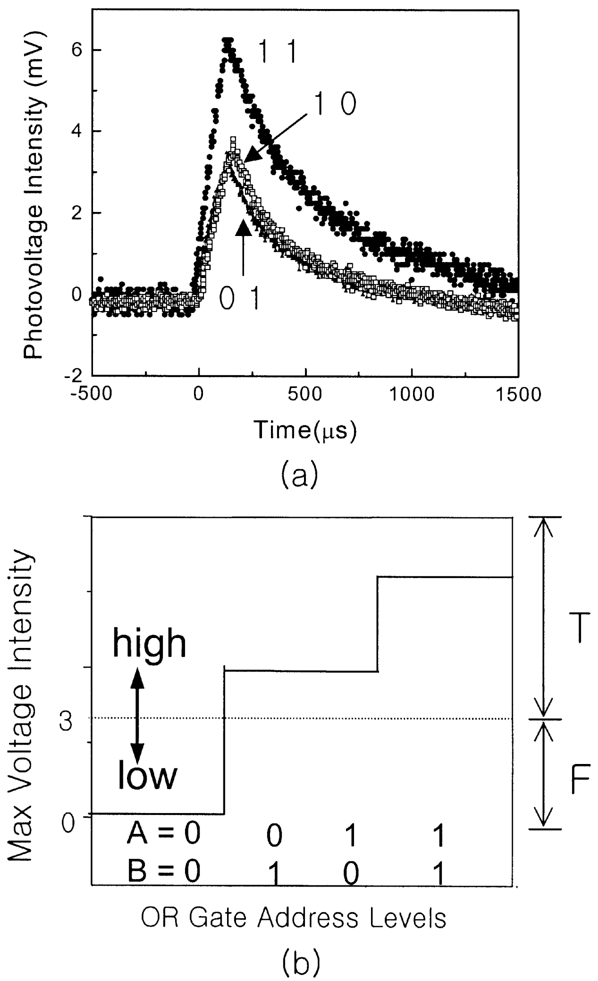

FIGURE 4 (a) The experimental photocurrent results, (b) photocurrent intensities corresponds to the AND gate address levels.

intensities of logically "1,1", "1,0", and "0,1" are about 6.1, 3.7, and 3.4 mV, respectively. Thus, the high photocurrent of "1,1" can be differentiated with low photocurrent "1,0" and "0,1" by the threshold below at 3 mV. Figure 4(b) shows the photocurrent intensities corresponds to the "OR" gate address levels. These result indicates that the high photocurrent intensity of both sides input "A and B" exhibits logically "True" or "1". And the low photocurrent intensity of single input "A" or "B" and no light input indicates logically "False" or "0".

CONCLUSIONS

In this study, the bio-logic gate device was fabricated by GFP/viologen/cytochrome *c* structured molecular photodiode. "OR" logic function of bio-logic gate device was investigated by using the laser pulse irradiation. Photocurrent intensities generated by laser pulse irradiation was separated by threshold into high and low current. The photocurrent intensity generated in single line input was lower than that of double line input. The high photocurrent intensity indicates "1,1" in truth tables and low photocurrent indicates "0,1" or "1,0". Finally, "0,0" input corresponds to a dark state without light generation. The "OR" logic gate function was successfully achieved based on high- and low-photocurrent by threshold.

Other bio-logic gates with "XOR" logic function can be fabricated by the modification of the array of the proposed biomolecular photodiode. The bio-logic gate device is similar in principle to diode-based wired-logic gate. A second challenge will be to scale down the size of the device and integrate molecular bio-logic gate with molecular-scale wires such as conducting DNA or carbon nanotube.

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