Nanoscale Biomemory Device consisted of Redox Protein

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ABSTRACT

The basic principles in development of new functional devices can be inspired from the biological systems such as molecular recognition, electron transfer chain, or photosynthetic reaction center. By mimicking organization of the functional molecules in the biological system, molecular electronic devices can be realized artificially. Because the basic paradigm for electronic information storage is retention of charge in a capacitor, the most straightforward approach to molecular scale memory would store charges at the molecular level. Another, more fundamental, approach would utilize the oxidation states of individual molecules to store charge. This technique has the advantage that multiple oxidation-reduction states within one molecule can be addressed to access multibit. Redox-active biomolecules have charged states at various potential. Application of a reducing potential causes the biomolecules to obtain electrons, resulting in a negatively charged monolayer. When an oxidizing potential is applied, electron-transfer returns the molecules to the neutral state. In this study, molecular information storage of self-assembled layer of spinach ferredoxin was investigated by applying the reduction potential as a write function and measuring the stored reducing charge as a read function.

KEYWORDS

nanoscale bioelectronic device, biomemory, ferredoxin, self-assembled layer, redox protein

INTRODUCTION

Biodevices, based on biomimetics, have emerged as a breakthrough with great potential for generating new concepts and technologies for the development of next generation electronics (Kaminuma, 1991; Nicolini, 1990; Aizawa, 1991; Cass, 1996). The main concept was inspired from the fact that individual biomolecules, especially proteins, could be used as the basic unit of an electronic device, so that the integration scale of the device could be increased by several orders of magnitude. The fervor related to biomolecule based electronics began in the early 1980s, and research groups related to the topics have subsequently emerged in the United States, Japan and Europe. The experts in the various fields, such as life science, physics, chemistry, chemical engineering, electronics and computer science, have begun collaboration on these fascinating research subjects, and opened the field of new hybrid technology. Biomolecule based electronics are not a single pathway of technological development, and are not in direct competition with any existing research projects in the race to develop a specific technological artifact. The difficulties of producing biomolecular electronic devices based on the biomimetics have certainly been acknowledged by all those involved, but the ideas and technologies of the life sciences and related fields have been actively employed to step to the next stage in the development of new functional devices.

BIOMOLECULAR DIODE BASED ON THE PHOTOSYNTHEIS

The transfer of an electron from one side of a molecule to the other, or between molecules, is one of the most fundamental and ubiquitous processes in electronic materials and biological systems (Kavarnos, 1993). The control and exploitation of this process in organized molecular systems is a major proposition for molecular electronics and bioelectronics (Kuhn and Hong, 1993). Progress in molecular
electronic devices engineering is still rather modest, due to problems associated with the elucidation and effective control of such structures and interactions at the nano level. Photoinduced electron transport processes in nature, such as photoelectric conversion and long-range electron transfer in photosynthetic organisms, are known to occur, not only very efficiently, but also unidirectionally, guided by molecular functional groups (Kavarnos, 1993; Deisenhofer et al., 1985). The concepts for the development of new functional electronic devices can be inspired from biological systems, such as the electron transfer chain or the photosynthetic reaction center. By mimicking the organization of the functional molecules in a biological photosynthetic system, artificial bioelectronic devices can be realized. In the initial process of photosynthesis, a biological electron transfer system, photoelectric conversion occurs, followed by long-range electron transfer, which takes place very efficiently in one direction through the biomolecules (Gust and Moore, 1989). The specific energy and electron transfer take place on a molecular scale, due to the redox potential difference and electron transfer property of the functional molecules; especially the electron acceptor, sensitizer and electron donor (Fujihira, Nichiyama, and Yamada, 1985).

Molecular films, fabricated by appropriate techniques, can be used as model systems for the corresponding photosynthetic reaction center in the biological system. In recent years, substantial interest has focused on thin film fabrication or the formation of biomaterials mono- and multi-layers on solid surfaces (Lvov, 1999; Choi et al., 2001a).

Based on these techniques, various artificial biomolecular devices have been fabricated to mimic the electron transport function of biological photosynthesis. Isoda et al. investigated a biomolecular photodiode composed of flavin-porphyrin hetero LB films and its optical and electrical characteristics (Isoda et al., 1992). They use Flavin and porphyrin as a sensitizer (S) and an electron acceptor (A), respectively. Fujihira et al. investigated an electrochemical photodiode that consisted of the Langmuir-Blodgett (LB) films of three functional biomolecules or an aligned triad on the electrode, which worked in electrolyte solution (Sakomura et al., 2002). Investigations of electron transfer between the electrode and the excited dye molecules were also carried out, in which ferrocene; pyrene and viologen were used as the electron donor (D), S and A units, respectively. The metal/insulator/metal (MIM) structured device, consisting of hetero-type LB films of D, S and A, was fabricated and the photoinduced electron transfer investigated (Sakomura et al., 2002). Recently, a biomolecular photodiode composed of electron D/S/Relay (R)/A type 4 component MIM devices has been investigated (Choi et al., 1998). Development of a biomolecular photodiode is important in the area of molecular electronics, as it can be applied to molecular memory devices due to its photoswitching and rectifying characteristics. Figure 1 shows schematic structure of MIM device, and photoswitching property of biomolecular photodiode.

A biomolecular photodiode, consisting of LB films of ferrocene, flavin, viologen and TCNQ as
the D, S, R and A units, respectively, was designed based on the photoinduced electron transport in a natural system (Fujihira, Nichiyama, and Yamada, 1985). By using two acceptor molecules (R and A), the time for the separated charge state (A⁻/R/S/D⁺) can be sustained longer than that of the A⁻/S⁺ hetero system. Charge recombination from R and A, to the ground state S, can be reduced due to the fast electron transport from S* to A, via R, and the increased distance between S and A in the presence of R. Based on these effects, the molecular photodiode composed of D/S/R/A hetero LB films is expected to show better diode and switching properties than those of S/A and D/S/A hetero LB films. By adding the D molecules, backward electron transport of excited S can be reduced, and by the addition of the R molecules, charge recombination from A to ground state S can be reduced. Choi et al. investigated biomolecular photodiodes using green fluorescent protein (GFP) and cytochrome c (Choi et al., 2001b; Choi et al., 2001c; Choi and Fujihira, 2004). Recently, researchers have investigated the nano-scale diode using scanning probe microscopy (SPM). Cui et al. investigated the scanning tunneling spectroscopy (STS) based current-voltage (I-V) measurement, and measured the single molecular conductivity of the organic SA layer (Cui et al., 2001). Khomutov et al. investigated the single molecular conductivity of cytochrome c LB layer by STS based I-V measurement (Khomutov et al., 2002). In our recent research, the biomolecular diode consisting of a chlorophyll a and ferredoxin heterolayer was investigated by STS based I-V characteristics. Figure 2 shows the rectifying property of biomolecular diode.

BIOMOLECULAR MEMORY

Since 1989, various concepts for molecular information storage have been proposed. In 1989, Hopfield et al. proposed the concept for the shift register memory, and Choi et al. investigated the shift register memory using the biomolecular hetero LB layer (Hopfield, Onuchic, and Beratan, 1989; Choi et al., 2001d). In 1991, Saito et al. proposed the fractal memory concept, and Choi et al. also investigated the fractal memory function of a biomolecular photodiode (Hirano et al., 1998; Saito and Sugi, 1991; Sugi and Saito, 1994; Choi et al., 2003; Roth et al., 2000). Lindsey et al. investigated a molecular approach for information storage (Gryko et al., 2000).
The basic principle of molecular information storage is to store charge in oxidation states of redox-molecules that are immobilized on a metallic surface. The advantages of the proposed molecular information storage are the molecular properties and dimensions, improved charge-retention times, multiple bits storage and low operating power. Molecular information storage enables the storage of tera bits of memory. Roth et al. also investigated the charge storage of an organic molecular monolayer using a 100µm sized micro electrode in an electrolyte solution (Roth et al., 2000; Gryko et al., 2000; Roth et al., 2003; Ambroise et al., 2000). Redox-active biomolecules have charged states at various potentials. Application of a reducing potential causes the biomolecules to obtain electrons, resulting in a negatively charged monolayer. When an oxidizing potential is applied, electron-transfer returns the molecules to the neutral state (Li et al., 2002).

Figure 3. Fundamental concept of biomolecular memory

In our recent study, biomolecular information storage was investigated by applying a reduction potential as a write function, and then measuring the stored reducing charge as a read function. The write function of biomolecular information storage was investigated by applying a reduction potential to the biomolecular layer by a chronomperometry (CA) measurement. The charge-retention characteristics of the biomolecular layers were determined using open circuit potential amperometry (OCPA). The details of the write (CA)-read (OCPA) experiment, and its use in the measurement of the retention charge of a biomolecular layer, are shown in figure 3.

The biomolecular information storage experiment was performed as follows. First, the biomolecular layer was reduced by the application of a reduction potential. Next, the applied potential
was disconnected from the electrode. During the disconnection time, the electrochemical cell relaxed to the OCP, after which, the applied potential was changed to match the determined OCP. The counter electrode was reconnected, and the resulting current monitored as the biomolecular layer was oxidized (because the OCP is at an oxidizing potential). The intensity of the observed current was proportional to the number of molecules that remained reduced while the counter electrode was disconnected. The charge retention was measured by changing the disconnect time, so that all the initially reduced biomolecules decayed back to the neutral state. In biomolecular information storage, the charge retention time of the reduced state is around 100 sec. Thus, applying a reducing potential every 90 sec is necessary to preserve the reduced (writing) state.

**CONCLUSION**

Biomolecular electronic devices have made some advances toward establishing strategies for the development of the molecular electronic device based on the photosynthesis. From our results, it is summarized that the proposed biomolecular electronic device, which mimics the biological photosynthesis, can be usefully applied in the future as new electronic devices, such as a molecular diode, molecular memory. Our next challenge is the real application and commercialization of the biomolecular electronic device. In our research, a basic biomolecular electronic device has been developed, and should now be extended to the construction of advanced electronic devices. These achievements lay the groundwork for further research on biomolecular electronics, which can help to overcome the limit of current electronic devices.

Throughout the research, we can acquire more scientific results that are the verification of scientific theory, application of various technological fields (biology, photonics, physics, and chemistry), and establishment of industrial base. Bioelectronic devices are not possible in common use and cannot make an industrial benefit immediately. However, considering present market demand and future prospect of electronics, Bioelectronic device's share may grow rapidly in 21th century. If the bio device could be early developed, it can secure monopolistic technological position in worldwide market. Ultimately, biodevices can establish new industry field coming from Biotechnology (BT)+Information technology (IT)+Nano technology (NT). Also, it is expected that the bioelectronic devices can contribute to stand the technological advanced country through the creation of high value industry which provide synergy and motive for society. The bioelectronic device typically requires very short time from research to commercialization. Thus, research introduced above should be achieved at early time.

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