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Photochemical Switching of Electrochemical Process by Spiropyran LB Films

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Photoelectrochemical control of the ion-blocking ability of the Langmuir-Blodgett (LB) film as an ion gate was demonstrated on a gold optically semi-transparent electrode (Au OTE) coated with multilayers containing photoresponsive amphiphilic compounds. When UV light was irradiated upon the modified Au OTE, this LB film became more compact to block permeation of ions into and out of the LB film and therefore inhibited electrochemical reactions of the redox active species in solution. On the other hand, when visible light was irradiated, this layer became more loose and redox species could penetrate the LB film.

The process of vision is an example of a light induced change in the properties of a bilayer membrane. There are three classes of photoresponsive membranes that can lead to pronounced changes in the behavior of membrane-building molecules. The first type of photoreaction involves a change in the cis-trans isomerizaton,[1,2] the second one is photoscission reaction,[3] and the third one involves a change in the hydrophilicity of the head group.[4-6]

In this letter, we will report the biomimetic visual system by using the last type of photoreaction of LB films. This device is composed of the gold optically semi-transparent electrode (Au OTE) modified with LB films containing photo-responsive amphiphiles in contact with a redox solution in a photoelectrochemical cell. In this device, photochemical reactions in the LB film caused by weak photo-irradiation trigger a large electrochemical current in a similar manner as in the visual system. The principle of the device is shown pictorially in Fig. 1.

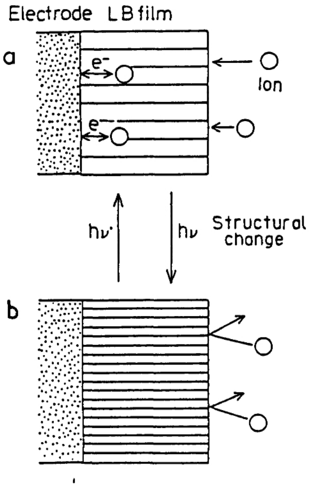

Fig. 1. Schematic representation of a biomimetic visual system, i.e. photochemical switching of electrochemical process by an LB film.
a, loose structure of LB film formed by hν' irradiation which allows ion-permeation and formation of electrical double layer and thus electrochemical reaction of redox active ions in solution.
b, compact structure of LB film formed by hν irradiation which blocks ion-permeation and inhibits electrochemical process.

A photoresponsive amphiphilic derivative and an ester of fatty acid used are shown in Fig. 2. 3',3'- Dimethyl-1'-hexadecyl-6-nitrospiro-(2H-1-benzopyran-2,2'-indoline) (SP) was synthesized in our labolatory according to the method reported by Guruda and Leblanc.7) G.R.-grade methyl arachidate (AME) was purchased from Tokyo Kasei Co. and was used without further purification. All other chemicals were G.R.-grade and used as received.

The measurement of surface pressure - area isotherms and the automated deposition of LB films on substrates were carried out with a Langmuir trough equipped with an electronic microbalance and a glass Wilhelmy plate (Kyowa Kaimenkagaku Co.). Monolayers were obtained by spreading a benzene solution of the amphiphiles on an aqueous subphase solution containing 0.05 mM $NaHCO_3$. Since a SP monolayer by itself was unstable, a mixed monolayer SP with AME (1:3) was used. The mixed monolayer formed at the air-water interface was deposited at 25 mN m^{-1} by the LB method. The horizontal lifting method was repeated 5 times for constructing multilayer on Au OTE's or quartz plates. The resulting multilayer is abbreviated as SPM. Photoelectrochemical properties of this LB device was investigated with a conventional three electrodes potentiostat. The Au OTE was mounted via a viton rubber "O"-ring against the cell window and served as the working electrode. The auxiliary electrode was a gold wire and the reference electrode was a saturated calomel electrode (SCE). The light source was a 500 W Xe lamp and Toshiba UV-D35 and Y-45 glass filters were used for isolating UV and visible light, respectively. The solution conditions for electro- and photoelectrochemical measurements were as follows: 10 mM $Fe_2(SO_4)_3$ solution containing a supporting electrolyte (0.1 M H_2SO_4) was placed in the electrochemical cell and was deaerated by bubbling purified nitrogen. All measurements were carried out at room temperature of ca. 25 °C.

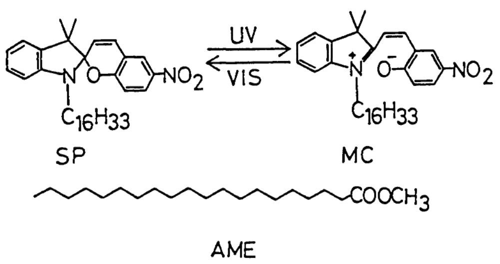

Fig. 2. Structural formulae of amphiphiles used.

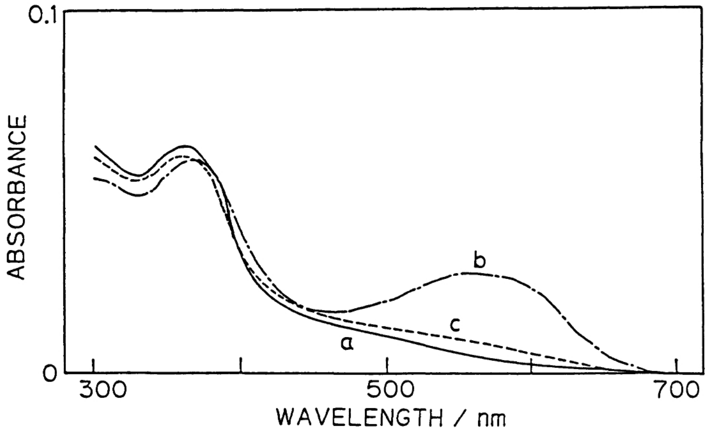

Fig. 3. Absorption spectra of the SPM on the quartz plate. a, a virgin film before light irradiation: b, after UV light irradiation for 30 s: c, after visible light irradiation for 60 s.

The absorption spectra of SPM deposited on the quartz plate are shown in Fig. 3. Spectrum (a) corresponds to the closed SP structure and spectrum (b) to the open merocyanine (MC) structure that was obtained by irradiating the SP with UV light for 30 s. Spectrum (c) was obtained by irradiating MC with visible light for 60 s, and shows that the SP form was recovered.[8)]

Figure 4 shows cyclic voltammograms (CV's) for Fe^{3+}/Fe^{2+} system obtained with three types of electrodes. An Au disk electrode, a naked Au OTE, and an Au OTE modified with SPM were used for curves (a), (b), and (c), respectively. The reversible and quasireversible redox waves of Fe^{3+}/Fe^{2+} can be seen in curves (a) and (b), respectively, while the very irreversible redox waves are seen in curve (c). The contamination on the surface of the Au OTE introduced during the Au vapor deposition might be a reason for the quasireversibility on the naked Au OTE, whereas the Au OTE modified with SPM hinders the redox reaction of Fe^{3+}/Fe^{2+} more drastically.

In Fig. 5 are shown CV's obtained with the Au OTE modified with SPM under UV and visible light irradiation and in the dark. Curve (a) shows the large current of Fe^{3+} ion reduction compared with others. The SPM in this state lacked the ability to block Fe^{3+} ions. Curve (b) shows CV under UV light irradiation. In this case the reduction current gradually decreased with time. This means that by UV light irradation SPM changed the structure, which resulted in the increase of the ability to block Fe^{3+} ions. Curve (c) shows that this ability was kept even after the UV light was switched off. Curve (d) shows CV under visible light irradiation. In this curve the current was increasing with time. The SPM changed the structure from MC to SP form again and Fe^{3+} and Fe^{2+} ions could penetrate the

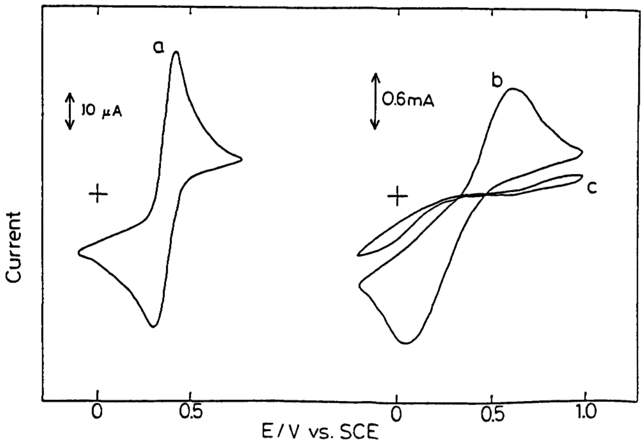

Fig. 4. Cyclic voltammograms of 10 mM $Fe_2(SO_4)_3$ aqueous solution containing 0.1 M H_2SO_4 under N_2 at a scan rate of 0.1 V s^{-1}. a, Au disk electrode (ca. 0.02 cm^2): b, naked Au OTE electrode (ca. 0.8 cm^2): c, Au OTE modified with SPM (ca. 0.8 cm^2).

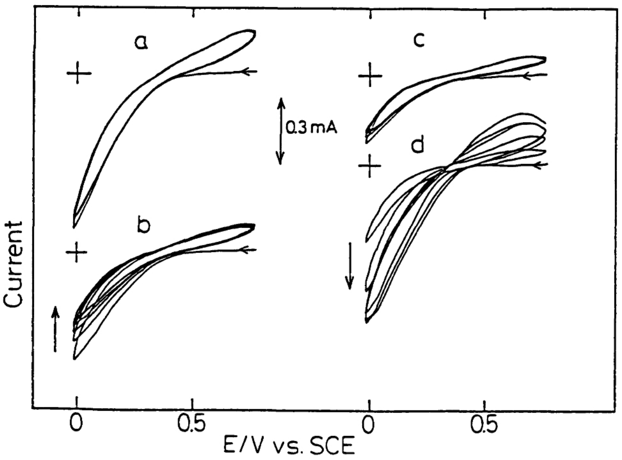

Fig. 5. Cyclic voltammograms on the Au OTE modified with SPM. Other conditions are the same as those in Fig. 4. a, in the dark: b, under UV light irradiation: c, in the dark after b: d, under visible light irradiation.

SPM more easily. In this manner, this LB device exhibits the ability to control the ion permeability and thus the electrochemical reactivity by UV and visible light irradiation (Fig. 1).

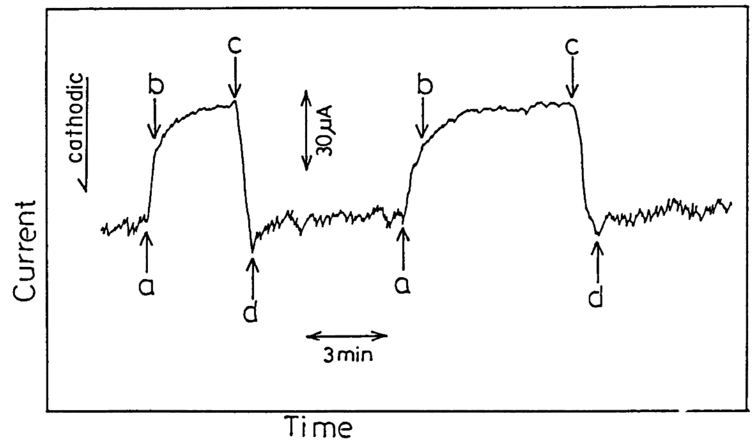

Fig. 6. Repeated photoresponses of reduction current on the same Au OTE modified with SPM as shown in Fig. 4 at a constant electrode potential (0.3 V vs. SCE). a, UV light on: b, UV light off: c, visible light on: d, visible light off.

In Fig. 6 is shown a time course of the photoresponse of the photo-initiated reduction current of Fe^{3+} ions at a constant electrode potential of 0.3 V vs. SCE. This figure also clearly exhibits that a biomimetic visual system, i.e. photochemical switching of the electrochemical process of electroactive species in solution was realized successfully. This enabled us to draw a large electrochemical current caused by the photo-initiated structural change in the LB membrane upon weak light irradiation.

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