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Characteristic Analysis of Molecular Photodiode Using Conducting Polymer(PANI) as An Electrode

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Molecular photodiode consisted of an electron acceptor(A), a sensitizer(S) and an electron donor(D) is fabricated by mimicking photoinduced electron transfer system in the biological photosynthesis. Polyaniline(PANI)-stearic acid(SA) composite LB films used as an electrode was deposited onto hetero-LB films of A/S/D stacked on ITO glass. The PANI-SA composite LB films exhibited high electrical conductivity of $10^{-1} \sim 10^{-2}$ S/cm upon with HCl or I_2 doping. Especially, iodine is found to be the most promising dopant, since it gives a remarkable stability for the molecular photodiode system. The rectifying characteristic and photoswitching function of the proposed molecular photodiode is introduced.

Keywords : Polyaniline; Langmuir-Blodgett film; Photodiode

INTRODUCTION

In the initial process of photosynthesis, energy conversion and electron transfer take place very efficiently due to the redox potential difference between functional groups of biomolecules^[1]. The fabrication of various artificial molecular device by mimicking the biological electron transport system have been reported.^[2,3]

In our previous work, we have fabricated the metal/insulator/metal (MIM) organic devices consisted of an electron donor (ferrocene), a sensitizer (pyrene), and an electron acceptor (TCNQ) by LB method, and investigated their photo-induced electron transfer properties.^[4, 5]

In the present study, the MIM organic devices using an electrically conductive PANI-SA composite LB film instead of Al electrode was fabricated in order to improve the stability of organic thin film and prevent

the effects of schottky barrier between organic compound and Al surface. We report some preliminary results on the preparation and properties of PANI-SA composite film, and photodiode.

MATERIALS AND EXPERIMENTAL

The PANI composite LB film is prepared using stearic acid as a surface active material with the Nima Model 2022 (Circular Type). The working, reference and counter electrodes are used with Pt, Ag/AgCl and Pt electrode, respectively. KI aqueous solution is used as the electrolyte. Electrical conductivity of PANI-SA composite LB films doped with HCl or I₂ was determined from the slope of I-V curve obtained using a Keithley 236 parameter analyzer by 2 probe method. The molecular photodiode was fabricated by depositing PANI-SA composite LB films doped with I₂ onto the hetero-LB films aligned on ITO glass in order of A/S/D. A schematic diagram of the apparatus for photocurrent measurement is shown in Figure 1. A 150W Xenon lamp(Oriel Co., USA) was used as a light source and the photocurrent was measured using Keithley 236 parameter analyzer.

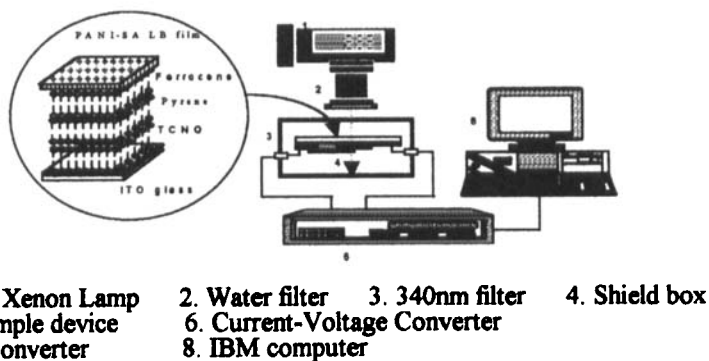


FIGURE 1. Schematic illustration of a hetero-type cell and experimental setup.

RESULTS AND DISCUSSION

The π -A isotherm for monolayer of PANI-SA composite LB film is shown in

Figure 2. The PANI-SA composite is able to form a stable, condensed monolayer. The limiting area estimated by extrapolating the steepest region of the condensed phase to zero pressure was $4 \sim 13 \text{ \AA}$.

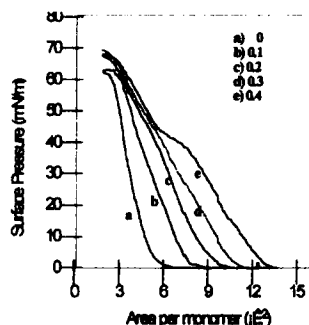


FIGURE 2. π -A isotherm of PANI-SA composite LB film under various weight fractions of SA

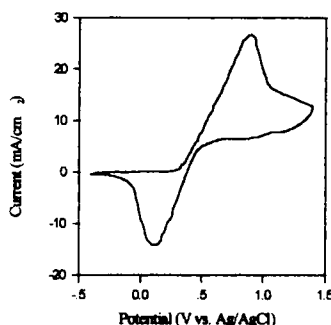


FIGURE 3. Cyclic Voltammogram of PANI-SA LB film doped with I_2

The cyclic voltammogram of PANI-SA composite LB film doped with I_2 is shown in Figure 3. During the scanning at positive potential, the anode current reached a maximum value at 0.8V. When the cyclic direction is reversed, the oxidized form of PANI-SA composite is reduced back to the original starting material at -0.4V. Thus, the redox potential of composite was determined as 0.5V

Electrical conductivity of PANI-SA composite LB film doped with HCl or I_2 is shown in Table 1. The PANI-SA composite LB films with high electrical conductivity of $10^{-1} \sim 10^{-2} \text{ S/cm}$ were obtained, and their conductivity revealed essentially a close value as that of conventional PANI HCl complex. Especially, iodine is found to be the most promising dopant, since it gives a remarkable stability for the application as a polymer electrode in the MIM molecular device consisted of A/S/D.

The photocurrent-time response caused by the stepped illumination of a 340nm UV monochromatic light is shown in Figure 4. When a positive potential is applied in accordance with the energy level in the MIM molecular device, a stable photocurrent is generated. With repeated step illumination, the reproducible photocurrent is obtained accordingly. The photocurrents are

very stable and the level was consistent during the repeated cycle over 30 minutes. The results indicate that the photoswitching

TABLE 1. Electrical conductivity of PANI-SA composite films doped with HCl or I₂

dopants	no	HCl	I ₂
conductivity(S/cm)	2.9×10^{-8}	1.7×10^{-1}	1.8×10^{-2}

function of the MIM molecular device is achieved. When the reverse potential is the applied, the photocurrent was much smaller than that of forward one. As shown in Figure 5., the rectifying characteristic is observed from the current(I)-voltage(V) measurement. In the proposed molecular device, the photo-induced unidirectional flow of electrons could be achieved due to the redox potential difference as well as electronic coupling between the functional molecules.

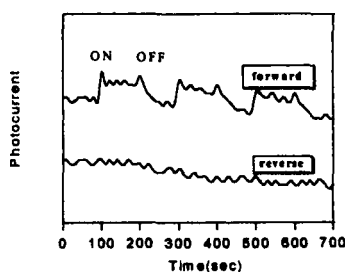


FIGURE 4. Photocurrent-time response of the molecular device

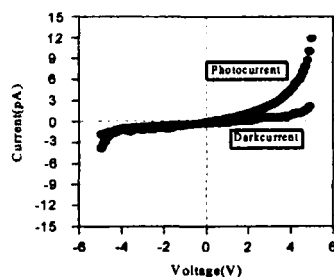


FIGURE 5. I-V characteristics of the molecular device

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