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Se Young Oh [a] , Joon-Kyu Park [b] , Jung Woo Choi [b] & Chan-Moon Chung [c]

[a] Dept. of Chem. Eng., Sogang University, Seoul, 121-742, Korea
E-mail:

[b] Dept. of Chem. Eng., Sogang University, Seoul, 121-742, Korea

[c] Dept. of Chem., Yonsei University, Wonju, 220-710, Korea

Version of record first published: 29 Oct 2010

To cite this article: Se Young Oh, Joon-Kyu Park, Jung Woo Choi & Chan-Moon Chung (2002): Fabrication of Micro Array of Polyimide LB Film and Its Application in Bioelectronics Device, Molecular Crystals and Liquid Crystals, 377:1, 241-244

To link to this article: http://dx.doi.org/10.1080/713738524

Mol. Cryst. Liq. Cryst., Vol. 377, pp. 241-244

1058-725X/02 $12.00 + .00
DOI: 10.1080/10587250290088997

Fabrication of Micro Array of Polyimide LB Film and Its Application in Bioelectronics Device

SE YOUNG OH[a], JOON-KYU PARK[a], JUNG WOO CHOI[a] and CHAN-MOON CHUNG[b]

[a]*Dept. of Chem. Eng., Sogang University, Seoul, 121-742, Korea and* [b]*Dept. of Chem., Yonsei University, Wonju, 220-710, Korea*
E-mail: syoh@sogang.ac.kr

Ultra thin film of a polyamic acid having benzene and sulfonyloxyimide moieties was prepared using a Langmuir-Blodgett (LB) technique and micro array pattern of the photosensitive polyimide LB film was obtained by a UV lithographic method. To array cytochrome c along the micro array pattern, the well-characterized monolayer of cytochrome c was immobilized on a gold electrode surface by self assembly technique. The redox activity and electron transfer between cytochrome c molecular center and electrode interface for the self-assembled cytochrome c monolayer were investigated through the cyclic voltammetry measurements. Also, its application in bioelectronic device was discussed.

Keywords: polyimide LB film; pattern; lithography; cytochrome c; immobilization; self-assembly; redox activity

INTRODUCTION

The ability to generate patterns of proteins and cells on solid surface is important for biological electronic technology, tissue engineering and fundamental study of biophysics. Especially, the techniques for micro pattern and immobilizing proteins along the pattern on gold surface

have been widely studied. However, some problems such as conformational change, random molecular orientation, the detachment of protein and the fragility of membrane resulting in less sensitivity and short longevity still exist. In this work, the micro array pattern of self-assembled cytochrome c using a mixed self-assembled monolayer of alkanethiolates was carried out with a conventional photolithographic technique as shown in Figure 1.

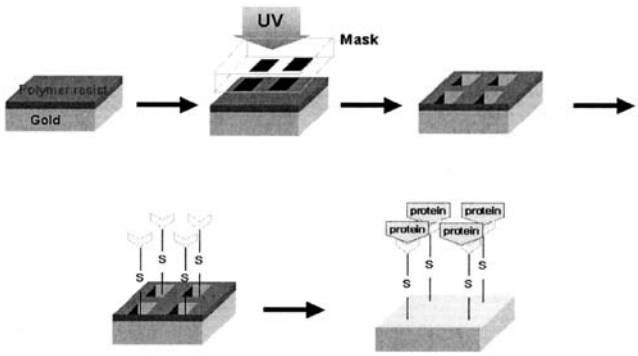

FIGURE 1 Patterning procedure of self-assembled cytochrome c monolayer.

EXPERIMENTAL

Polyamic acid was synthesized by condensation polymerization of N, N'-dihydroxybenzenetetracarboxylic amic acid and 2,6-naphthalenedisulfonyl chloride. The detailed synthetic procedure and photodegradation behavior of polyimide were reported in the previous publications [1,2]. A 200 μl chloroform solution of the polyamic acid was spread on deionized water and π–A isotherm was measured at a barrier speed of 5 cm^2/s at 25 . The polyimide LB film was prepared by the thermal treatment of the precursor at 200 for 1h. After exposure of the film with 254 nm deep UV light, the gold substrate was developed in THF solvent. And then cytochrome c was immobilized on the patterned gold substrate using a mixed self-assembled monolayer of alkanethiolates. The mixed self-assembled monolayer was prepared by

immersing the patterned gold substrate into mixed ethanolic solutions of 11-mercaptoundecanoic acid (MUDA, 1mM) and decanthiol (1 mM). The carboxylic group of 11-MUDA allowed the cytochrome c to form self-assembled monolayer. The photoirradiation of polyimide film was conducted with an exposure system of Spectral Energy Co. equipped with a 500 W high-pressure mercury lamp in conjuction with a narrow band pass filter for 254 nm. The patterned surface of self-assembled cytochrome c was observed using an atomic force microscope (Park Scientific Instruments, Auto Probe CP). Electrochemical properties of self-assembled cytochrome c monolayers were investigated from the measurements of cyclic voltammetry (Zahner Elektrik, IM6 system).

RESULTS AND DISCUSSION

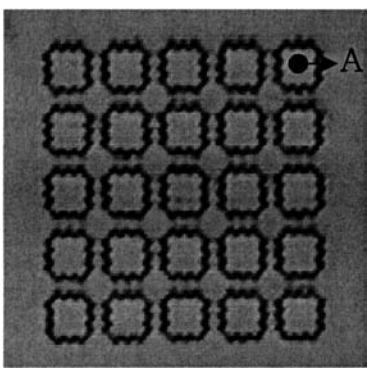

FIGURE 2 Positive-tone image of LB film upon 254 nm UV light irradiation of 25 mJ/cm^2

A positive-tone image of polyimide LB film was shown in Figure 2. The micro array pattern, of which side length of square was 2 μm, was obtained at a dose of 25 mJ/cm^2. It can be noted from the result that the polyimide film is an effective positive type resist material for obtaining high lithographic resolution. Figure 3 showed the changes in AFM images of patterned surface, which is the point A in figure 2, after immobilizing cytochrome c. The uniform and dense surface morphology of self-assembled cytochrome c monolayer was observed. Figure 4 showed the relationship between redox peaks and decanthiol contents for the cyclic voltammograms of self-assembled cytochrome c immobilized with a mixed monolayer of 11-MUDA and decanthiol. It

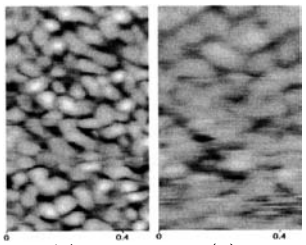

FIGURE 3 Changes in AFM images of the surface patterned; (a) before (b) after immobilizing cytochrome c

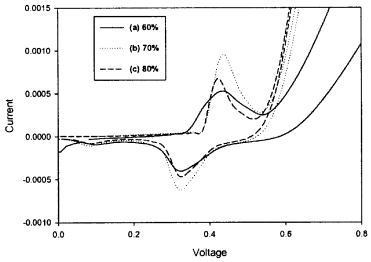

FIGURE 4 Cyclic voltammograms of cytochrome c immobilized on a gold electrode modified with mixed monolayer. $HOOC(CH_2)_{10}S$ contents ; (a) 60 %, (b) 70% and (c) 80%.

has been found that cytochrome c prepared with a mixed monolayer containing 70% of 11- MUDA had a high electrochemical activity. The carboxyl group plays role in specific binding site for the cytochrome c molecule. The alkanethiolate functions as a spacer between the functionalities. As a consequence, it can be concluded that the self-assembly of cytochrome c using a mixed monolayer containing alkanthiolate was effective and the fine micro array pattern of self-assembled cytochrome c was achieved by a conventional photolithographic technique.

Acknowledgement

This work was supported by the National Program for Super Intelligence Chip of the Ministry of Commerce, Industry and Energy as one of the new technology of next generation and University Research Program of the Ministry of Information and Communication.

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