Modulation of Photoinduced Transmembrane Currents in a Fullerene-Doped Freestanding Lipid Bilayer by a Lateral Bias

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ABSTRACT: We report on a novel lipid bilayer system, in which a lateral bias can be applied in addition to a conventional transmembrane voltage. Freestanding bilayer lipid membranes (BLMs) doped with [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) were formed in a microaperture, around which metal electrodes were deposited. Using this system, it was possible to modulate and amplify photoinduced transmembrane currents by applying a lateral bias along the BLM. The results indicate that the microfabricated Si chip with embedded electrodes is a promising platform for the formation of transistor-like devices based on PCBM-doped BLMs and have potential for use in a wide variety of nanohybrid devices.

INTRODUCTION

The bilayer lipid membrane (BLM), a main component of cell membranes, can be formed by a self-assemble process. Such membranes are ultrathin, with thicknesses of only 3–5 nm, and, at the same time, demonstrate an ultrahigh ionic resistance (>100 Ω). The BLMs can be readily functionalized by incorporating nanomaterials into them and can be used in various biological applications. For example, BLMs containing ion channel proteins have been utilized in biosensing and biological applications;[1–7] α-hemolysin protein has been incorporated into BLMs to form a nanosized hole for DNA and RNA decoding.[8–10] and ultrashort carbon nanotubes have been inserted into BLMs for molecular sensing and selective ion transport.[11–13] Recently, nanohybrid optoelectronic devices prepared by using a combination of photosensitive nanoparticles and BLMs have attracted considerable interest. BLMs functionalized with gold nanoparticles, have been demonstrated to show reversible photoresponses.[14] We also previously reported that an organic semiconducting material, [6,6]-phenyl-C61-butyric acid methyl ester (PCBM), can be used to dope BLMs to form a photodetector-like device.[15] In solid-state semiconductor technologies, the gate bias is usually used to regulate and magnify the current flowing through the semiconductors. It is possible to further improve the performance of BLM-based devices by introducing a “gate bias” to the BLM system.

Here, for the first time, we report that the performance of nanohybrid devices based on BLMs can be modulated by applying a lateral voltage to fullerene-doped BLMs. We fabricated a novel BLM system in which a lateral bias voltage inside the BLM can be applied. We then investigated the effect of the bias voltage on photoinduced transmembrane currents.

RESULTS AND DISCUSSION

Si chips having a circular microaperture were fabricated, according to the procedures previously described.[2] To apply a lateral voltage to the BLMs, two metal electrodes were formed on Si chips using the process shown in Figure 1. The center of the metal mask was first carefully aligned with the aperture of the chip (Figure 1a) under a microscope. A layer of aluminum (Al) with a thickness of 30 nm was then thermally evaporated through the metal mask (Figure 1b). As a passivation layer to prevent direct contact between metal electrodes and aqueous solutions, a thin layer of SiO2 was then sputtered at the center part of the chip (Figure 1c). The two edge regions of the Al layer were exposed for use as electrical contacts. Finally, a fluoropolymer CYTOP was cast to cover the Si side of the chip, as described previously (Figure 1d).[2] Photographs of the fabricated Si chip and a microscopic image of the electrodes are shown in Figure 1e,f, respectively. The diameter of the aperture was 40 μm and the distance between the two electrodes was 30 μm. The electrodes reached the edge of the
aperture to ensure that an effective lateral bias was applied to the BLMs. The final Si chip was then silanized by treating with 2% (v/v) (tridecafluoro-1,1,2,2-tetrahydrooctyl) dimethylchlorosilane in anhydrous toluene for 6 h at room temperature in a nitrogen-filled glove box.

The experimental setup for measuring the transmembrane photoresponse under lateral bias is illustrated in Figure 2. The Si chip with Al electrodes was used as a support for forming BLMs by applying the so-called “folding” method, as reported previously.1,2,16 Solvent-free BLMs were formed across the microaperture from diphytanoyl-sn-glycero-3-phosphocholine (DPhPC) solution with and without PCBM, as described in a previous report.15

We first investigated the formation of BLMs across the microfabricated apertures around which Al electrodes and SiO2 passivation layers were deposited. Only the Si chips in which the resistance between the two Al electrodes in air was over 200 GΩ were used for the experiments to confirm that there was no leakage current through the surface or the bulk of the Si chip. After BLM formation, the resistance across the BLMs, as measured between the two Ag/AgCl electrodes, was in excess of 200 GΩ, showing that highly resistive BLMs were formed, even when the additional Al and SiO2 layers have been deposited around the microaperture. The resistance between the two Al electrodes was still in excess of 200 GΩ after the BLM formation, indicating that the thin SiO2 layer acted as an insulating layer, electrically separating the Al electrodes from the buffer solutions.

To understand how a lateral bias applied to the Al electrodes can affect the electrical characteristics of a BLM, we measured the resistance and the capacitance of the BLMs (recorded between the two Ag/AgCl electrodes) under different lateral alternating current (AC) bias conditions. To reduce the noise due to the AC bias source, a homemade battery-powered AC source (11.8 kHz sine wave) was connected to the two Al electrodes. As shown in Figure 3a, when the AC bias was increased from 0 to 3 V (peak to peak), the resistance across the BLM remained essentially constant at over 200 GΩ, indicating that the application of a lateral bias did not weaken the ability of the BLM to function as a barrier to ion permeation. On the other hand, the capacitance of the BLM

Figure 1. (a)–(d) Scheme showing the fabrication process of the Si chip with electrodes. The size of the chip is 5 mm × 23.8 mm. Photograph of the Si chip and a microscopic image of the electrodes are shown in (e) and (f).
decreased with increasing lateral bias \((n = 6)\). It is possible that the lateral AC bias could change the ion distribution around the BLM, or change the dipole potential of BLM, leading to a reduction in capacitance.\(^{17,18}\) However, further studies will be needed to confirm this assumption. We also recorded the electrical characteristics of PCBM-doped BLMs under different lateral AC bias values. As shown in Figure 3b, the resistance of the PCBM-doped BLMs under an AC bias was similar to that of BLMs composed of only DPhPC lipid, implying that the PCBM molecules did not affect the high resistance of the BLMs under an AC bias. The capacitance of the PCBM-doped BLMs decreased with increasing lateral bias \((n = 3)\), showing the same trend as the capacitance of pure BLMs. However, it should be noted that the capacitance of the PCBM-doped BLM was measurably lower than that of the pure DPhPC BLM.

Since the PCBM-doped BLMs are photosensitive,\(^{15}\) it is possible to form a phototransistor-like device by using the lateral bias to regulate the photocurrent. Therefore, we also measured the transmembrane photocurrent of the hybrid membrane under an AC bias. Figure 4a shows the photoresponses of the BLM composed of pure DPhPC under repeated illumination and different lateral bias. Under a lateral bias of \(0−3\) V, immediately after the light was switched on, the transmembrane current showed a transient positive shift, followed by gradual downward decay. After the light was switched off, the transmembrane current demonstrated a reverse trend, first a negative shift and then a gradual upward decay. The current did not reach a steady state within the 1 s period of illumination under lateral bias (\(1−3\) V). When the light was turned off, the transmembrane current immediately returned to its original light-off value. The current response upon illumination (difference between light-off and light-on currents) increased from 11.6 to 39.4 pA with an increase in the lateral bias from 1 to 3 V. As shown in Figure S2, the averaged current response, as calculated based on three experiment cycles, was positively correlated with the applied lateral bias, indicating that the lateral bias regulates and amplifies the transmembrane current. In the absence of a lateral bias, as shown in Figure 4b, the transmembrane current exhibited a gradually decaying upward shift upon illumination, which is similar to that of the nondoped membrane. The slower positive transient could also be attributed to the larger capacitance without the lateral bias than at higher lateral voltages (see Figure 3b). These results demonstrate that a phototransistor-like device could be formed based on free-standing hybrid BLMs.

The mechanism responsible for regulating the current by a lateral bias is still not clear. It appears that PCBM or lipid molecules are not structurally altered under a lateral bias, since no transmembrane leakage of pure and PCBM-doped BLMs was detected, as shown in Figure 3. Therefore, the modulation of photoresponse could be attributed to the effects of light illumination and the lateral electric field that is simultaneously applied to the PCBM-doped BLMs. It has been reported that the photoluminescence and absorption of CdSe nanoparticles that are incorporated into a polymer film would be changed due to the external electric field.\(^{16}\) Similar behaviors have also been observed in other systems that comprise nanoparticles.\(^{20−22}\) Therefore, we conclude that the electrical field introduced by the lateral Al electrodes in our experimental setup may have altered the optical characteristics of the PCBM molecules in the BLMs, leading to a phototransistor-like transmembrane current response that is regulated by the lateral bias. More detailed experiments will be needed to confirm the proposed mechanism, which would include comparing the absorption/photoluminescence spectra of the hybrid membranes under different lateral bias values and measuring the distribution of membrane potential using fluorescent labels.

### CONCLUSIONS

We fabricated a Si chip equipped with two metal electrodes as the support for BLMs. It was confirmed that the additional electrodes and insulating layers around the aperture of the Si chip did not affect the characteristics of the BLMs formed on them. When the lateral bias was applied to the two electrodes on the Si chip, the nondoped and PCBM-doped BLMs maintained high resistance. However, as the lateral bias increased, the capacitance of the BLMs reduced. Without PCBM incorporation, the BLM did not demonstrate a clear response to light illumination or lateral bias. On the other
hand, the PCBM-doped BLM showed photoresponse under light illumination and lateral bias. We were able to modulate the transmembrane current by changing the lateral bias. These results indicate that the BLM is a promising platform for hybrid nanodevices.

**EXPERIMENTAL SECTION**

**Materials and Methods.** DPhPC and PCBM were purchased from Avanti Polar Lipid Inc. and Frontier Carbon Corporation, respectively. The BLMs were formed in symmetrical buffer solutions (2 M KCl, 10 mM 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid, pH 7.2 with KOH), where two Ag/AgCl electrodes were placed at each side. After the BLM formation, current recordings were performed using an Axopatch 200B patch-clamp amplifier (Molecular Devices). The resistance across the BLMs was calculated based on the currents observed at the transmembrane voltage of ±100 mV and ±100 mV. Capacitance was measured by applying transmembrane ramp voltage pulses of 1 V/s at a holding potential of 0 mV. The BLMs were then repeatedly illuminated by means of an LED light with a center wavelength of 850 nm (Solis High Power LED, Thorlabs) with on and off times of 1 s, which was controlled by a multifunction generator (WF1974, NF Corporation). The applied voltage at the vertical direction during the measurement was ±1 V unless otherwise specified.

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