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Transparent conductive oxide electrode dependence of photocurrent characteristics in bacteriorhodopsin photocells

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ABSTRACT

We investigated the photocurrent characteristics in photocells using bacteriorhodopsin (bR) thin films deposited on various kinds of transparent conductive oxide (TCO) electrodes. The photocurrent depends largely on the species of TCO and partly on the surface morphology. The photocell using a bR thin film deposited on a fluorine-doped tin oxide electrode with a textured structure showed the largest photocurrent. Our results indicate that the variation of capacitance near the interface induced by the bR's light-driven proton pump function affects the transient photocurrent, while the capacitance near the interface is produced by the TCO electrode, bR thin film, and electrolyte solution.

1. Introduction

Bacteriorhodopsin (bR) is a protein containing a covalently bound retinal chromophore, found in the purple membrane of *Halobacterium salinarum*. bR releases protons into the extracellular side of the cell with light absorption and takes up protons on the cytoplasmic side of the cell, in which processes bR experiences a photochemical cycle, passing through a series of intermediate states [1]. It is therefore well known that bR exhibits a proton-pump function induced by photo-irradiation [2]. In addition to its unique functionality, bR has long-term stability against various environmental factors, such as pH and temperature. Utilizing these properties, applications of bR such as elements for neural network architecture, holographic imaging, photonic logic gates, and biomolecular electronics, have been proposed [3–9]. Photo-sensor devices with bR thin film, which show the transient photocurrent signal in association with the light-driven proton pump function, have been demonstrated [10,11].

To date, the casting or spin–casting technique, Langmuir–Blodgett (LB) technique, electro-phoretic deposition technique, sedimentation under a direct-current (DC) bias, and electrostatic layer-by-layer self-assembly technique were used to deposit the bR thin film or immobilize bR on the electrode [8,12]. We used a dip-coating technique to prepare the bR thin film [13–15], which allows not only an efficient film-formation of purified bR but also a relatively easy formation of a uniform thin film. We recently proposed a bR-based bipolar photosensor device, utilizing the bR thin films patterned on two indium tin oxide (ITO) electrodes and the electrolyte solution [15].

In this letter, we investigated the transient photocurrent characteristics in photocells consisting of bacteriorhodopsin (bR) thin film by the dip-coating technique on various kinds of transparent conductive oxide (TCO) electrodes, such as indium tin oxide (ITO), fluorine-doped tin oxide (FTO) with or without a textured structure, and indium-, gallium-, or aluminum-doped zinc oxide (IZO, GZO or AZO). Tin oxide electrode without doping was used in past years [16–18], and ITO has been used in a vast majority of cases of transient photocurrent analyses [19–24], while gold was used occasionally [25,26]. On the other hand, various TCOs are available recently since they have been employed in applications such as flat-panel displays, light emitting diodes, and solar cells [27–31]. On these circumstances it is interesting to investigate the transient photocurrent characteristics in photocells having bacteriorhodopsin (bR) thin film deposited on various kinds of TCOs. We used wild-type bR and genetic mutant bR-D96N for this study. So far, systematic studies on transient photocurrent characteristics on various TCOs both for wild-type and D96N bR thin films have not been performed. We found that the magnitude of the transient photocurrent signal in wild-type and D96N bR photocells depends strongly on the TCO electrode species and partly on the surface morphology, and the photocell having the wild-type or D96N bR thin film prepared on the FTO electrode with a textured structure showed the largest photocurrent. Our study provides insight into

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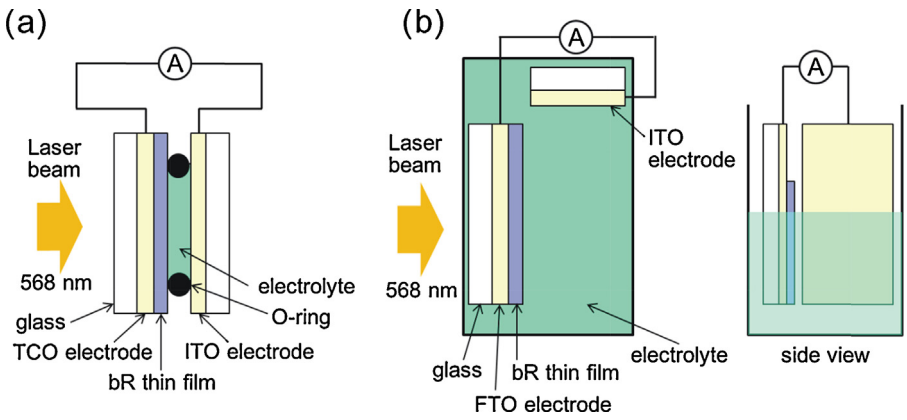

Figure 1. (a) Typical photocell structure. One electrode substrate was a TCO substrate with a bR thin film, and another counter-electrode was a bare ITO substrate. An electrolyte solution (KCl, 0.2 M, pH 7.2) was enclosed with an O-ring (1.9-mm-thick and 9.8 mm_{ϕ} inner-diameter). The area by the inner-diameter of the O-ring is the laser irradiation area. The two electrode substrates were fixed so as not to spill the electrolyte. (b) Different type of photocell structure. An FTO substrate with a bR thin film and bare ITO substrate were immersed in an electrolyte solution (KCl, 0.2 M, pH 7.2) in a small cuvette. The two electrode substrates were located perpendicularly to each other. The area 20 mm × 15 mm of the bR coated FTO substrate was immersed in the electrolyte solution. Similarly, the laser irradiation area is about 10 mm_{ϕ}.

the origin of transient photocurrent, and the data obtained indicate that the variation of capacitance in the interface region, which is induced by the bR's light-driven proton pump function, leads to the transient photocurrent as a capacitive current. The capacitance in the interface region is produced by the TCO electrode, bR thin film, and electrolyte solution including the electrical double layer. Finally, we show that this study leads to improvement in the efficiency of the transient photocurrent characteristic and flexibility of the electrode geometry in bR photocells.

2. Experimental

The purple membrane of a wild-type bR was obtained from *Halobacterium salinarum* strains, about which we described in detail previously [13–15]. The D96N mutant was obtained in accordance with the procedure of Mescher and Strominger [32] and Krebs et al. [33] Briefly, the D96N gene, in which Aps (D) 96 in pMPK85 (plasmid) was mutated to Apn (N), was obtained through site-directed mutagenesis. A *Halobacterium salinarum* strain (MPK409) was transformed by the D96N gene, and a D96N mutant was obtained through homologous recombination. We referenced the methods of Oesterhelt and Stoeckenius [34] and of Becker and Cassim [35] for incubation and purification to obtain purified purple membranes of wild-type bR and D96N bR.

For dip coating we prepared a purified purple membrane suspension, in which purple membrane fragments of wild-type bR or D96N bR are included in a 10 mM Tris–HCl buffer with pH of 7.2. The concentration of the bR suspension was about 5 mg protein/ml. The absorption spectra of the bR suspension were measured using a UV–vis spectrometer. The peak wavelengths of the absorption spectra were around 570 nm both for the purple membrane suspensions of wild-type and D96N bR. We prepared six kinds of different TCO substrates: ITO with a sheet resistance of 10 Ω/sq (Geomatec), FTO of 13 Ω/sq (TEC15, Aldlich), FTO with a textured structure of 12 Ω/sq (Type-U, Asahi Glass Co. Ltd.), IZO of 20 Ω/sq (Geomatec), GZO of 20 Ω/sq (Geomatec), and AZO of 32 Ω/sq (Geomatec). A precleaned substrate with a UV–ozone cleaner was dipped into the purple membrane solution in a cuvette and withdrawn at speeds ranging 0.04–15 mm/s. The film thickness generally depends on the concentration and viscosity of the solution and the withdrawal speed [36]. If the concentration and viscosity are the same at an ambient temperature, the film thickness is proportional to the square root of the withdrawal speed. We previously confirmed the relation for a solution of a purple membrane of wild-type bR and to some extend were able to control the bR film thickness through the withdrawal speed [15]. In this study, the wild-type or D96N bR film thicknesses ranged 100–200 nm for higher withdrawal speeds (1–15 mm/s), which was estimated by using differential interference contrast microscope or scanning electron microscope (SEM) observation of the cross-section of the thin films.

Photocells using wild-type or D96N bR thin film prepared through the dip-coating technique were fabricated, and we then evaluated the photocurrent characteristics of their time response to photo-irradiation. The typical photocell's structure was described previously [15]. Figure 1 shows the photocell structures used in this study. Figure 1(a) shows a typical photocell structure, which consists of a TCO substrate with a bR thin film, a bare ITO substrate, and an electrolyte solution (KCl, 0.2 M, pH 7.2). Figure 1(b) is a different type of photocell structure, wherein an FTO substrate with a bR thin film and bare ITO substrate were immersed in an electrolyte solution (KCl, 0.2 M, pH 7.2) in a small cuvette and the two electrode substrates were placed perpendicularly to each other.

We used an optically pumped semiconductor laser with a wavelength of 568 nm (Sapphire 568, Coherent, Inc.) as a light source. An acousto-optic modulator, controlled by a function generator, enabled us to turn on and off the laser irradiation to a photocell, and a beam expander was used to adjust the laser irradiation area to be about 10 mm_{ϕ}. Since we irradiated the photocells at the laser power of 30 mW, the power density is 38 mW/cm^2.

3. Results and discussion

Figure 2(a) shows the photocurrent characteristics of the wild-type bR photocells with the geometry in Figure 1(a) with the bR thin film/textured FTO and bR thin film/ITO deposited at a withdrawal speed of 10 mm/s. It shows a typical time-differential photocurrent response in accordance with the turning on/off during photo-irradiation. The photocurrent flowed in the direction of the cathode from the electrode on which the bR thin film was immobilized when the light was turned on, and in the direction of the anode when the light was turned off. We found that the photocell with the bR thin film/textured FTO showed three to four times larger transient photocurrent response than the conventional photocell which uses the bR thin film/ITO, as seen in many studies [15,19–23]. Figure 2(b) shows the absolute peak value of the transient photocurrent flowing with the turned-on photo-irradiation for the wild-type bR photocells that have the geometry of Figure 1(a) with the bR film/various TCOs deposited at different withdrawal speeds. The dip coated film thickness is generally proportional to the square root of the withdrawal speed [36], as