

Article

Photovoltaic sensibility of optical biosensor produced by flexible and stretchable rubber utilized physical paradigm of solar cell

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Abstract: It is expected that the physical paradigm of solar cells will be possible to fabricate optical biosensors that mimic the human eye, including flexibility and stretchability. The purpose of this article is to demonstrate the morphological fabrication of an optical biosensor made of rubber by utilizing the physical paradigm of solar cells involving electric and chemical processes. However, a critical problem of current solar cells is their use of pieces of solid transparent conductive glass as electrodes, as especially shown in organic thin-film type solar cells involving dye-synthesized and perovskite-type solar cells. Therefore, we must solve this problem in order to be able to develop flexible and stretchable solar cells for optical biosensors. The key point of the solution is to avoid using rigid conductive glass and to coat a flexible and stretchable material such as rubber with TiO₂. In the present study, we proposed a novel fabrication technique for a flexible and stretchable rubber coated with TiO₂ by electrolytic polymerization utilizing our developed magnetic responsive intelligent fluid, hybrid fluid (HF), in order to produce the optical biosensor. The photovoltaic results experimentally demonstrated the photovoltage response to illumination with around 3–60 mV enhancement. In addition, we elucidated the photovoltaic mechanism by using electrochemical measurement involving the cyclic voltammetry (CV) profile and electrochemical impedance spectroscopy (EIS), introducing the equivalent electric circuit's intrinsic structure. The results demonstrated that the rubber type behaves dominantly in the area outside the electrical double layer (EDL) under illumination, and then the response time of photovoltage to illumination is slow with non-linear CV profiles. On the other hand, the optical biosensor type behaves dominantly in the EDL under illumination, and then the response time is fast with linear CV profiles, which denotes that the optical biosensor type is optimal for photodiodes. Furthermore, these results can demonstrate the chemical-photovoltaic reaction of the HF rubber involving TiO₂. The investigation might present the viability of the fabrication of ophthalmological systems that mimic the human eye.

Keywords: optical biosensor; rubber; stretchability; TiO₂; electrolytic polymerization; hybrid fluid (HF); electrochemical impedance spectroscopy; cyclic voltammetry; chemical-photovoltaic reaction

1. Introduction

It is important to expand the investigation into bioinspired robotics, whose purpose is to function in the same way as certain human biological features [1]. Such robotics must have multifunctional, autonomous, and power-efficient principles to allow them to perform as if they were natural living systems. Outcomes can be demonstrated by biological materials designed to function in the way that the five senses and nerves do in humans [2]. For example, cybernetic prosthetics, in which flexible organic sensory micro mechanisms mimic the auditory, optical, and nerve

responses of human organs, are expected to be highly efficient and to have widespread applications in rehabilitation [3]. They can also assist the able-bodied and improve healthcare through medical robotics. Bioinspired materials and electronics must be as soft and flexible as human tissue in order to be biocompatible in vivo [4]. Mechanical biocompatibility is achieved by using a structured artifact that morphologically mimics the motion and displacement of the human organs and tissues, while chemical biocompatibility is achieved by utilizing soft materials such as hydrogels, conductive materials such as carbon nanotubes (CNTs), and polymers such as polyimide (PI) or polydimethylsiloxane (PDMS). The flexibility and stretchability of these materials are significant in fabricating biocompatible systems because they provide haptic feedback in response to stimulation, and their reactions provide pertinent information in response to varied changes in the ambience [5]. Sensors react to their surroundings and are categorized according to whether they respond mechanically, electrically, optically, or chemically [6]. Sensors that meet the prerequisites of flexibility and stretchability to simulate tactile, gustatory, olfactory, auditory, and optical sensations are morphologically fabricated as artificial devices and systems: tactile sensation has been achieved with electronic skin (e-skin) [7,8]; gustatory and olfactory systems have been developed to respond to the taste [9] and aromas of various beverages and foods [10]; auditory sensations [11] and sensations related to equilibrium, especially inclination [12], have been incorporated into artificial biosensors for prosthetics, robotics, and other human aids. In addition, our innovative sequential studies on tactile, gustatory, olfactory, and auditory sensations confirm that artificial fabricates mimicking human sensory receptors are reactive to haptic, thermal, gustatory, olfactory, auditory, and inclination stimuli [13]. Flexibility and stretchability can be achieved by utilizing rubber in the artifacts, and conductivity and the solidification of artifacts such that stimuli are acquired as electric signals can be realized by our proposed cutting-edge technology of electrolytic polymerization. However, vision was not addressed by using the technique until recently. Therefore, in the present study, we examine artificial vision utilizing rubber and the developed electrolytic polymerization technology.

The physical and chemical paradigms, such as material and morphological fabrication of solar cells, are effective in achieving optical sensing. And then, we focus here on the current investigations into the development of solar cells related to the ophthalmologic sensory systems. Many different materials for the development of ophthalmologic feasibility have been proposed, including two-dimensional optoelectronic materials with photodetector arrays that generate photocurrent [14–17], organic and inorganic hybrid materials with perovskite such as solar cells [18–20], materials with CNTs [21], and organic materials conjugated with donor-acceptor heterojunction [22,23]. Regarding morphological fabrication, the cardinal issue is how to transmit the electric current, that is, how to generate voltage in the materials. Therefore, it has also been proposed to synthesize photovoltaic materials including donor and acceptor for electrons [24], transparent indium tin oxide (ITO) glass [25], the agent of p-poly(3,4-ethylenedioxythiophene)-pol(styrene sulfonate) (PEDOT:PSS), zinc oxide (ZnO) [26] and titanium dioxide (TiO₂) materials, etc., in the optical biosensor. These optical biosensors are semiconductors like photodetectors [27] with the result that the principles that apply to solar cells might be applicable. In

general, the predominantly used solar cells are silicon-type or compound-type, structured by a solid material. In contrast, organic solar cells, which are expected to increase efficiency, are categorized as dry- or wet-type: the former are perovskite solar cells (PSCs), as the ordinary performance characterizes the enhancing efficiency and the stability [28–30], and the latter are dye-synthesized solar cells (DSSCs), as the ordinary performance characterizes the tractability and the development [31–33]. However, the perovskite material in PSCs and the ITO transparent glass in DSSCs are solid, and these solar cells therefore do not meet the prerequisites of flexibility and stretchability for bioinspired sensors. And then, proposals have been made for flexible solar cells fabricated as thin film [34] or structured with a fiber configuration through which light can be transmitted [35,36]. Photonic materials involving elastomeric cores, dyes [37], or photonic crystals [38] have been utilized in fiber configurations. As in other cases whose fabrication is different from DSSC, the solar cell combined with semiconducting quantum dots made of ZnO has been proposed [39]. However, these materials yield solar cells that are flexible but not stretchable. In addition, in DSSCs, a photocatalyst is needed for the photovoltaic effect. This is achieved by coating the transparent ITO glass with a thin layer of TiO_2 by deposition under heating conditions. The deposition technique is necessary because TiO_2 particles are sintered to be conjugated by baking them on the glass so that photoexcitation occurs on the TiO_2 . In contrast, electrons are not emitted from TiO_2 if the TiO_2 particles are aligned or agglomerated without sintering. Therefore, a novel technique is required to create a sintered body of TiO_2 on a flexible and stretchable surface such as rubber.

Normal solar cells, such as organic thin-film type solar cells involving dye-synthesized and perovskite-type solar cells, have a solid transparent glass coated with TiO_2 . In order to coat TiO_2 on transparent glass or thin film, the powder of TiO_2 must be melted by heating. In contrast, the rubber is optimal for producing the flexible and stretchable solar cell. However, the rubber is also melted or burned out by using the same technique of coating TiO_2 on the rubber. Therefore, a novel technique is needed to be proposed. We proposed a different technique from the normal coating of TiO_2 on the solid material by utilizing chemical reactions and electrolytic polymerization.

In the present study, we utilized a rubber for the feasibility of the photovoltaically effective surface and proposed a novel technique that creates a sintered body of TiO_2 on the rubber without deposition or baking for the development of a flexible and stretchable optical biosensor that is applicable to organic ophthalmologic systems such as the retina of the human eye. For the reason that referring to the physical paradigm of solar cells involving electric and chemical processes can aid the novel technique, we elucidated the electric and chemical systems of our proposed optical biosensor.

The novelty of the present study is that we propose a technique that is different from the normal coating of TiO_2 on a solid material and that is applicable to coating TiO_2 on rubber by utilizing chemical reactions and electrolytic polymerization. The current study's objectives and limitations are to establish a novel technique. Therefore, the critical findings of the present study are the feasibility of the production of flexible and stretchable material coated with TiO_2 by utilizing rubber, which is substituted for a solid transparent glass. In addition, by using electrochemical measurements involving CV and EIS, we elucidated how the flexible and stretchable material produced with rubber instead of the solid material is characterized by illumination.

The production of solar cells made with flexible and stretchable material has crucial meaning for engineering development involving wearable solar cells, such as clothes, installing an isolated power unit by solar cells, etc.

2. Optical biosensor

2.1. Materials

In order to produce an optical biosensor with flexibility and stretchability related to the state-of-the-art solar cell, we used our proposed cutting-edge magnetically responsive colloidal fluid, hybrid fluid (HF), which was developed from our proposed magnetic compound fluid (MCF) to be compounded in rubber to enhance conductive sensibility. MCF can be produced easily by compounding a magnetic fluid (MF). MF includes 10 nm magnetite particles (Fe_3O_4) coated by a surfactant of oleic acid and 1 μm -order metal particles such as Ni or Fe. The developed HF consists of Fe_3O_4 particles, surfactant (sodium hexadecyl sulfate aqueous solution ($\text{C}_{16}\text{H}_{33}\text{NaO}_4\text{S}$)) is commonly used instead of oleic acid), water, kerosene, silicone oil (Q), and polyvinyl alcohol (PVA). PVA induces emulsion polymerization among water, kerosene and Q. By compounding water, kerosene, Q and PVA, HF can easily be compounded with any fluid and any type of rubber, including diene and non-diene rubbers. Furthermore, HF rubber (which is a compound of HF and a rubber) makes it possible to create artificial bio-inspired sensors mimicking human sensory cutaneous receptors such as free nerve endings, Merkel's disks, Krause end bulbs, Meissner corpuscles, Ruffini endings, and Pacinian corpuscles [40]. On the other hand, MCF rubber (which is a compound of MCF and a rubber) makes it possible to create solar cells such as DSSCs [41]. Thus, HF rubber has high potential in the production of optical biosensors.

In order for TiO_2 as a photocatalyst to be conjugated on the HF rubber, we apply electrolytic polymerization to electrolytes involving a metal complex with Ti as a hydrate [42]. Our previous studies have demonstrated that HF rubber can be vulcanized without sulfur by electrolytic polymerization [13,40]. HF rubber compounded with titanium potassium oxalate dihydrate ($\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$) solution (which can be dissolved in hydroxylamine (NH_2OH)) is electrolytically polymerized. By using electrolytically polymerized HF rubber involving a metal complex with sodium tungstate dihydrate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$) as a hydrate, we can not only make the rubber permeable and able to infiltrate liquids but also adhere a metal to the rubber, as demonstrated in our previous studies [13,40]; very thin electric wires can be adhered to the rubber to extract an electric signal from the rubber sensor.

Following the HF rubber production procedure (**Figure 1a**) and using the ingredients shown in **Table 1** with electrolytic polymerization of the HF rubber latex (**Figure 2a**), we obtained a solidified HF rubber coated by TiO_2 (**Figures 2b–2e**). In the present study, we used chloroprene rubber (CR) to produce an optical biosensor. When we use natural rubber (NR), as in the case of MCF, the rubber mixed with $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ solution solidifies before electrolytic polymerization due to its chemical reaction. We applied an electric field with a constant 10 V and 2.7 A between stainless steel plates with a 1-mm gap for 5 min under the application of a constant 188 mT magnetic field created by neodymium permanent magnets between the electrodes. The chemical process of the produced TiO_2 is described below. As

demonstrated in the MCF rubber, because vulcanized rubber grows from the anode side, the surface of the HF rubber on the anode side is flat, while on the cathode side, it has a concave-convex surface that reflects the chip of the rod-like magnetic clusters structured by the Ni and Fe_3O_4 particles. These particles assemble magnetic clusters by applying a magnetic field to enhance the conductivity of HF rubber, whose behavior is the same as that of MCF rubber. **Figure 3** shows scanning electron microscope (SEM) images of the produced HF rubber. The surfaces of both the anode and cathode sides were confirmed to have the expected configuration for Ni and Fe_3O_4 particles with TiO_2 , which appears as white dots in the figure. Furthermore, the configuration shows the high intensity of Ni and Fe and the low intensity of Ti, as measured by SEM elemental analysis. TiO_2 particles seem to be produced by the $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ solution; their production can be confirmed by X-ray photoelectron spectroscopy (XPS) showing a-rays from aluminum, as shown in **Figure 4**. Here, the C1s core level value of 285 eV was used to calibrate the energy scale, and the Ti2p spectrum was normalized. The peak at 465 eV is attributed to the 2p_{1/2} orbital of Ti, and that at 459.3 eV to the 2p_{3/2} orbital of Ti. XPS (Thermo Fisher Scientific K. K., Japan) has 50–400 μm spot size by X-ray sources of Al K α -ray operated at maximum 72 W, the energy range of 200–4000 eV, and 60 mm $\times$ 60 mm size of the analyzed area. SEM involving EDX (Hitachi High-Tech AW Cryo Inc., Japan) has 30-Pa pressure maintained in the analyzing chamber, 203-mm maximum size of the analyzed area, and 15-kV application voltage. These peaks are more prominent in the case of the anode surface than in that of the cathode surface. The presence of TiO_2 is confirmed on both surfaces. In general, TiO_2 is created by electrolytic polymerization on the anode side, however, HF rubber involving $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ is highly porous, which allows TiO_2 to be produced on the cathode side as well. Therefore, TiO_2 can also be coated on the surface of the rubber at the cathode side so that the creation of TiO_2 is occurred through the pores in the rubber. By analyzing the surfaces of the rubber at the anode and cathode sides with energy dispersive X-ray spectroscopy (EDX) as shown in **Figure 5**, W and K are produced on the surface of the rubber at the anode side more than on that at the cathode side. The results denote that $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ solutions are reacted predominantly on the surface of the rubber at the anode side more than on that at the cathode side. Here the EDX results were obtained in any areas as shown in **Figure 3**. Therefore, seen from the equations of the chemical-photovoltaic reactions as shown in the following section, at the anode side TiO_2 is created through $\text{Ti}(\text{OH})_2$, that is created by OH^- and $\text{TiO}(\text{C}_2\text{O}_4)^{2-}$ into which $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2$ is broken down. Consequently, the photovoltaic effect by TiO_2 on the surface of the rubber at the anode side is more than that on the surface of the rubber at the cathode side. Here, the size of our obtained TiO_2 by the present production technique is proved the level of several μm diameter by inducing with the SEM results. In case identifying accurately the distribution of the size of TiO_2 , we must use a particle size distribution analyzer. However, when we must rake the grains of TiO_2 from the surface of the produced HF rubber, the original formation of the particles cannot be remained. Because at the time of raking the TiO_2 particles they are broken. They are adhered mutually among them, and between the grains and the rubber by the present electric-chemical reaction. In addition, because our objective of the present study is the feasibility of the production of TiO_2 by the novel technique and the suitability for the

optical sensor, the distribution must be investigated with contriving without breaking the grains in another work.

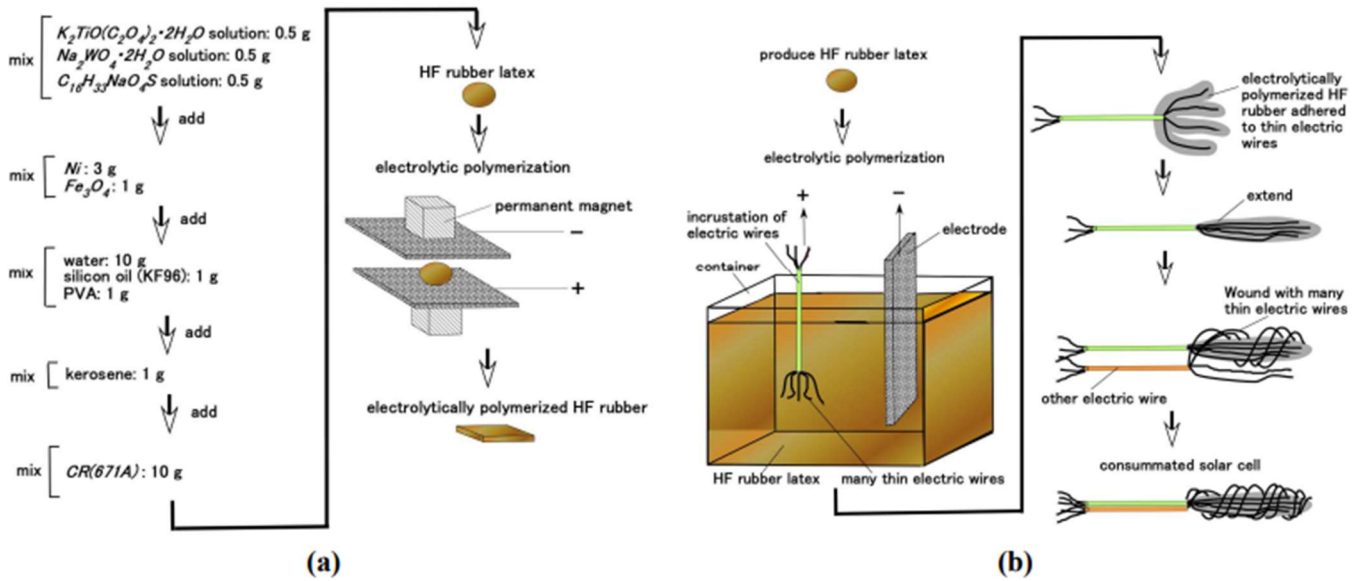


Figure 1. Procedure for the production of HF rubber and optical biosensor (a) HF rubber; (b) optical biosensor.

Table 1. Ingredients of HF rubber latex for optical biosensor.

Constituent	Weight [g]
K ₂ TiO(C ₂ O ₄) ₂ ·2H ₂ O solution (K ₂ TiO(C ₂ O ₄) ₂ ·2H ₂ O (90 wt%, Fujifilm Wako Chemical Co., Ltd., Osaka, Japan): 1 g; NH ₂ OH (50 wt%, Fujifilm Wako Chemical Co.): 10 g)	0.5
Na ₂ WO ₄ ·2H ₂ O solution (Na ₂ WO ₄ ·2H ₂ O (99.7 wt%, Fujifilm Wako Chemical Co.): 1 g; water: 10 g)	0.5
C ₁₆ H ₃₃ NaO ₄ S solution (C ₁₆ H ₃₃ NaO ₄ S (2.5 wt%, Fujifilm Wako Chemical Co.): 1 g; water: 10 g)	0.5
Ni (No. 123, Yamaishi Co., Ltd., Noda, Japan; µm-order and pimple-like shapes on the surface)	3
Fe ₃ O ₄ (Fujifilm Wako Chemical Co.)	1
Water	10
Silicon oil (KF96 with 1-cSt viscosity, undiluted solution, which would solidify Q; Shin-Etsu Chemical Co., Ltd., Tokyo, Japan)	1
PVA (98 wt%)	1
Kerosene (undiluted solution)	1
CR latex (671A, undiluted solution; Showa Denko Co., Ltd., Tokyo, Japan)	10

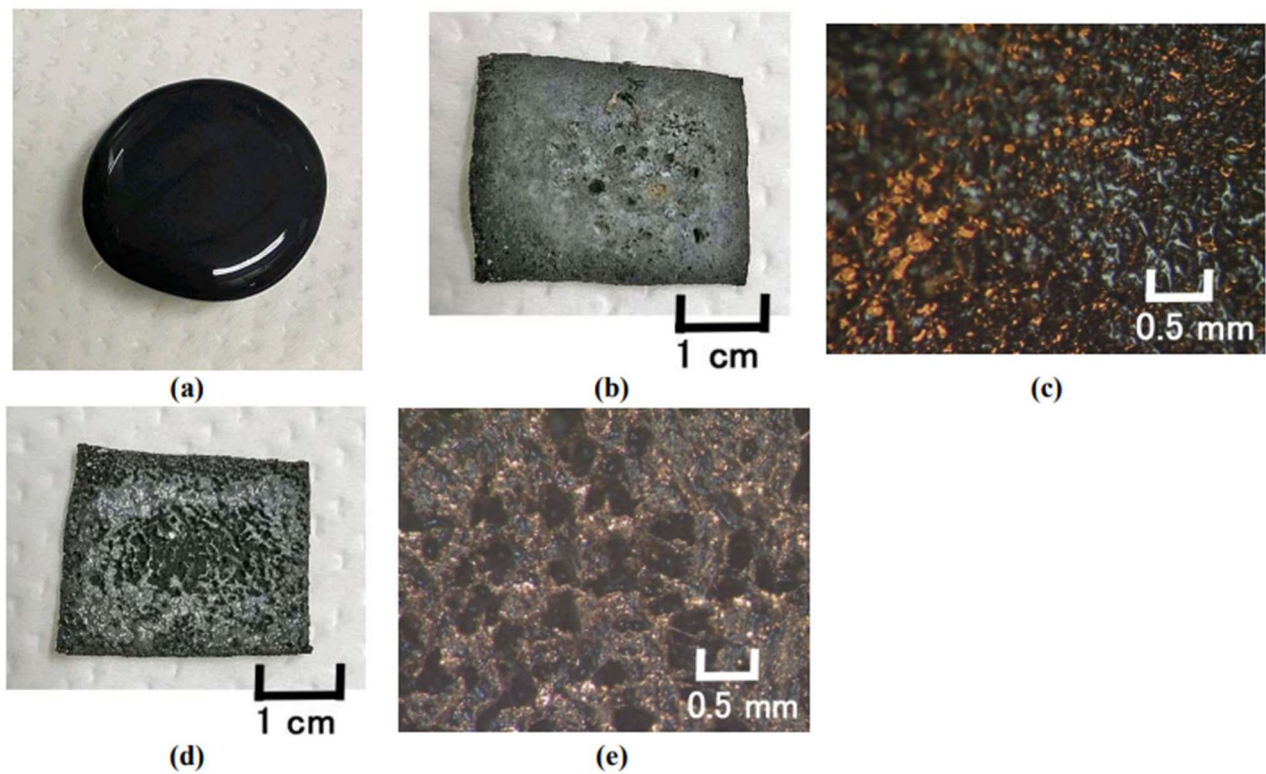


Figure 2. Images of HF rubber latex and electrolytically polymerized HF rubber: (a) HF rubber latex; (b)–(e) surfaces of the electrolytically polymerized HF rubber; (b) and (c) for anode side; (d) and (e) for cathode side. Images (c) and (e) show the surfaces of the HF rubber in (b) and (d), respectively, magnified by microscope.

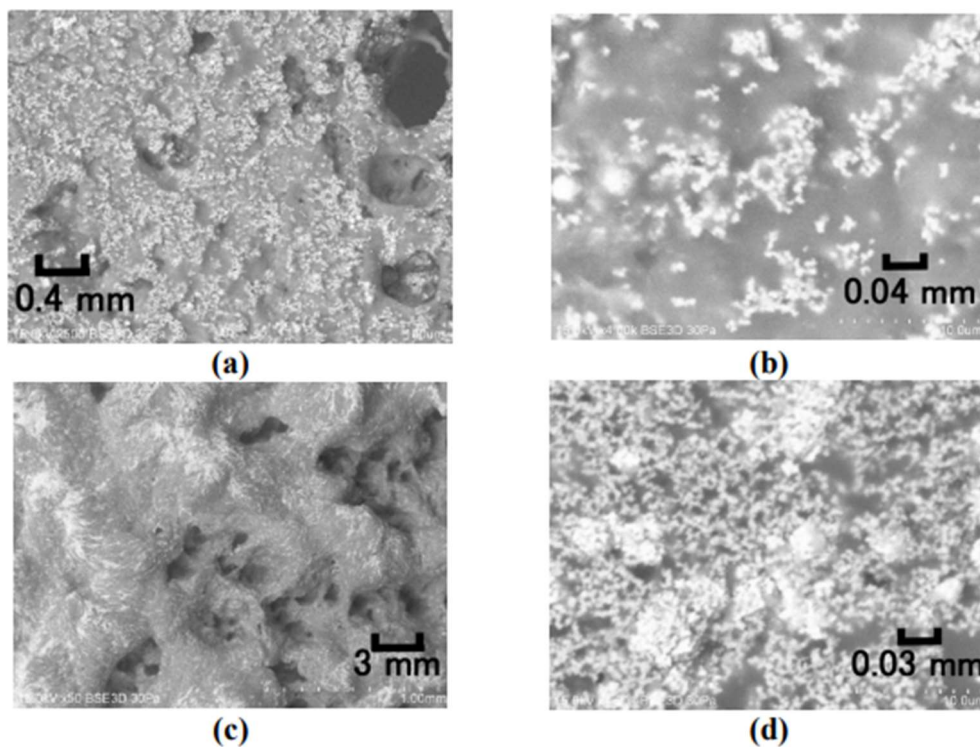


Figure 3. Scanning electron microscope (SEM) images of electrolytically polymerized HF rubber: (a) and (b) surfaces of the HF rubber (anode side); (c) and (d) surfaces of the HF rubber (cathode side); (b) and (d) magnified images of HF rubber surfaces shown in (a) and (c), respectively; (a) 500 $\times$ magnification, (b) 4000 $\times$, (c) 50 $\times$, (d) 4000 $\times$.

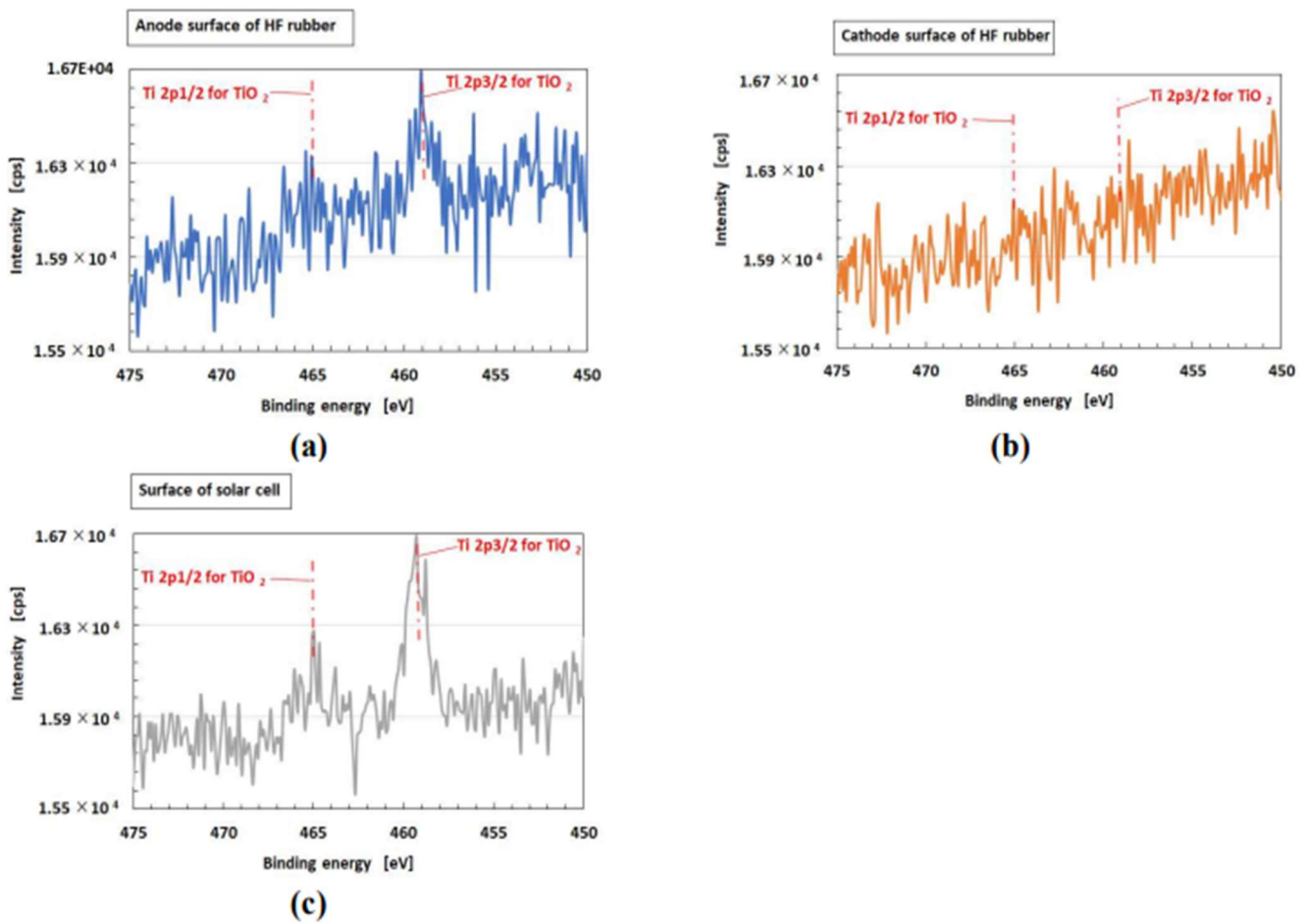


Figure 4. Images of electrolytically polymerized HF rubber by XPS: (a) surface of the HF rubber (anode side); (b) surface of the HF rubber (cathode side); (c) surface of the optical biosensor.

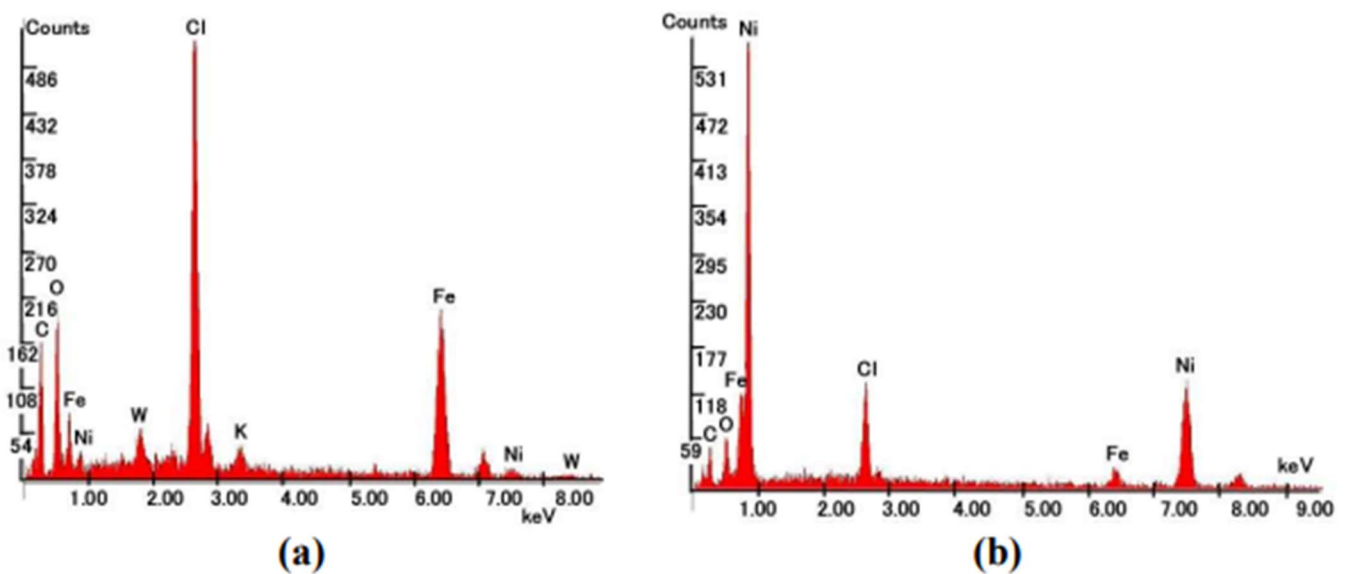


Figure 5. Energy dispersive X-ray spectroscopy (EDX) images of electrolytically polymerized HF rubber: (a) surface of the HF rubber (anode side); (b) surface of the HF rubber (cathode side).

2.2. Optical biosensor

Our using electric wire (**Figure 6a**) is comprised of seven extremely thin silver-gilt electric wires approximately 0.1 mm in diameter, and an outer plastic cover approximately 0.8 mm in diameter. To produce an optical biosensor as shown in **Figure 1b**, HF rubber with TiO_2 is solidified by the electrolytic polymerization and adhered to thin electric wires (for an anode electrode), as shown in **Figure 6b**. The opposing electric wires (for a cathode electrode) are wound around the solidified HF rubber (**Figure 6c**). By eliminating light on the solidified HF rubber, the electrons generated from TiO_2 flow between the anode and cathode electric wires. This is the consummated optical biosensor. Detailed SEM images of the surface of the HF rubber are shown in **Figures 6f** and **6g**. The configuration of Ni and Fe_3O_4 particles involving TiO_2 appears in white. XPS confirms that TiO_2 has been produced from $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ solution (**Figure 4c**). It is interesting that the peaks at 465 eV by $\text{Ti}2\text{p}_{1/2}$ and at 459.3 eV by $\text{Ti}2\text{p}_{3/2}$ are clearer in case of the optical biosensor (**Figure 4c**) than in the case of the HF rubber (**Figures 4a** and **4b**).

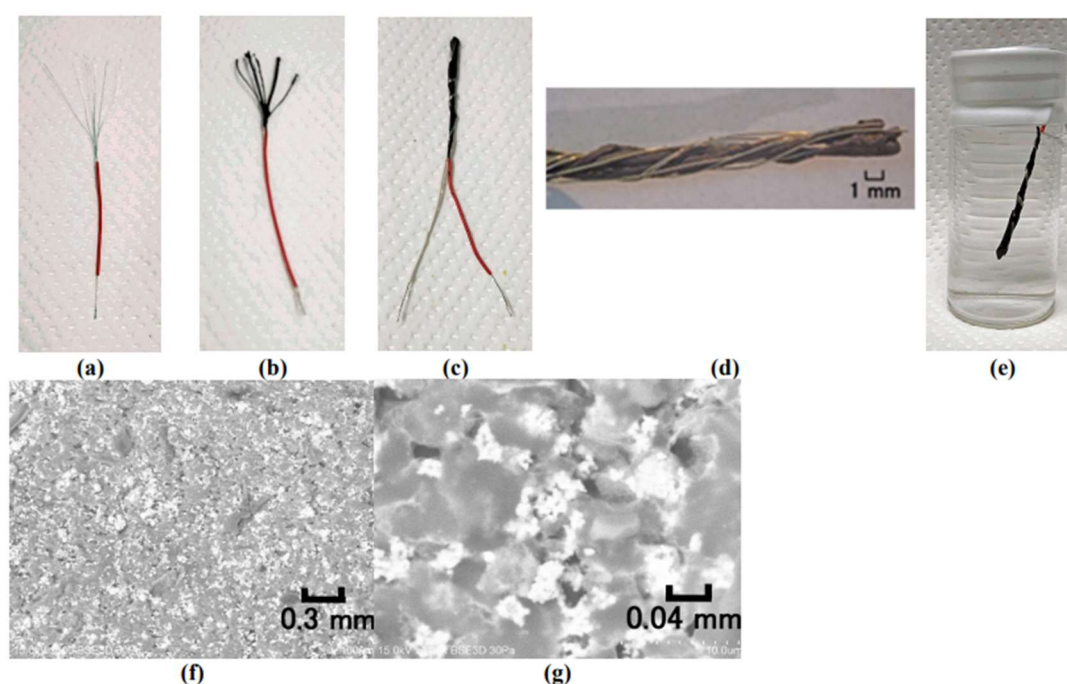


Figure 6. Images of HF rubber for optical biosensor: (a) electric wires before production; (b) electrolytically polymerized HF rubber adhered to thin electric wires; (c) electrolytically polymerized HF rubber wound around opposing electric wires; (d) detail of the chip of electrolytically polymerized HF rubber wound around the opposing electric wires; (e) completed optical biosensor; (f) surface of the electrolytically polymerized HF rubber of the optical biosensor; (g) magnified surface of the electrolytically polymerized HF rubber shown in (f); (f) 500 $\times$ magnification, (g) 4000 $\times$.

To make the optical biosensor durable for avoiding the aridity by air exposure, it must be retained wet by immersion in water, as shown in **Figure 6e**. The present state-of-the-art optical biosensor corresponds to the optic systems of the human eye, with the fabricated optical biosensor (**Figure 6c**) corresponding to the retina and the water (**Figure 6e**) to the vitreous body. It is needed to pay attention that the performance of

the fabrication of the optical biosensor as shown in **Figures 6c** and **6e** is the same as that of the ophthalmologic biosensor.

2.3. Experimental procedure

Ultimate goal of our study is to clarify the feasibility of the fabrication of the optical biosensor with utilizing the technical paradigm of our proposing production of state-of-the-art solar cell. Therefore, in the present study, we primarily investigate the response of the optical biosensor to the illumination and the physical and chemical structure of the intrinsic configuration of the optical biosensor, except for the detail investigation of the ordinary photovoltaic property of solar cells such as voltage-current relation, etc.

In order to investigate the reaction of the electrolytically polymerized HF rubber and the optical biosensor to illumination, the experimental apparatus shown in **Figure 7a** was used, with visible light (from 32700 lux to 44600 lux) or ultraviolet (UV) light (2400 lux, 375-nm peak wavelength). The voltage was measured by voltage meter (PC710; Sanwa Electric Instrument Co., Ltd., Tokyo, Japan). The optical biosensor consisted of the circuit shown schematically in **Figure 7b**. The electrons are created from TiO_2 by illumination and transferred between the thin electric wires. The thin electric wires outside of the HF rubber correspond to the ordinary transparent conductive glass plate coated with TiO_2 in DSSCs. The present optical biosensor is so efficient that the solid transparent conductive glass and TiO_2 coating are not used.

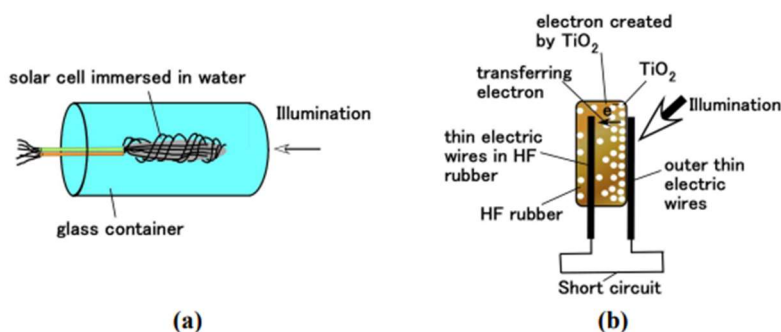


Figure 7. Schematic diagram of the present optical biosensor: **(a)** positioning of the optical biosensor in relation to illumination; **(b)** photovoltaic circuit of the optical biosensor.

On the other hand, regarding the elucidation of the physical and chemical structure of the intrinsic configuration of the optical biosensor, to investigate the photo-chemical reactions of the electrolytically polymerized HF rubber and the optical biosensor, the intrinsic structure of the materials was analyzed by cyclic voltammetry (CV). We measured the relation between the electric current I and voltage V , using a potentiostat (HA-151B; Hokuto Denko Co., Ltd., Tokyo, Japan) at a 50-mHz scan rate in the potential domain of -0.5 to 0.5 V. In addition, an inductance/capacitance/resistance (LCR) meter (IM3536; Hioki Co., Ltd., Ueda, Japan) was used to measure the electric properties involving impedance, inductance, etc. Additional electric properties were measured by electrochemical impedance spectroscopy (EIS).

The measurement apparatuses of voltage meter, potentiostat and EIS instrument have inner 0.1% accuracy.

3. Results and discussion

3.1. Experimental photovoltaics

Figure 8 shows the reaction of the photovoltage to illumination. Comparing **Figures 8a** and **8b**, the voltage in the rubber-type sample shows a gentle smoothing in the degree of the rising and falling edges of the voltage curves. Here we have already confirmed that the results by the repetition a few times were the same as the ones of **Figure 8**. In contrast, the sensor-type sample shows sharp changes in the degree of the rising and falling edges of the current or voltage curves. These patterns are shown schematically in **Figure A1** in Appendix. The degree of the rising and falling edges of the voltage curves denote the response time for irradiation. Namely, the response time in **Figure 8** means the period from the time when the voltages of HF rubber and HF optical biosensor respond by the illumination to the time when they are saturated to constant, which are schematically featured in **Figure A1**. In general, in the case of wet-type solar cells such as DSSCs, the voltage curves show a delay to irradiation because of the oxidation-reduction reaction. Therefore, the voltage curve of the rubber type is similar to that of DSSCs, in that the oxidation-reduction reaction is large. On the other hand, the response time is minimal enough for sharp voltage curves to appear in the rising and falling edges. This phenomenon can be seen in photodiodes. Therefore, the sensor type has a large response to illumination and approximates the behavior of photodiodes. The ramifications of this are discussed below.

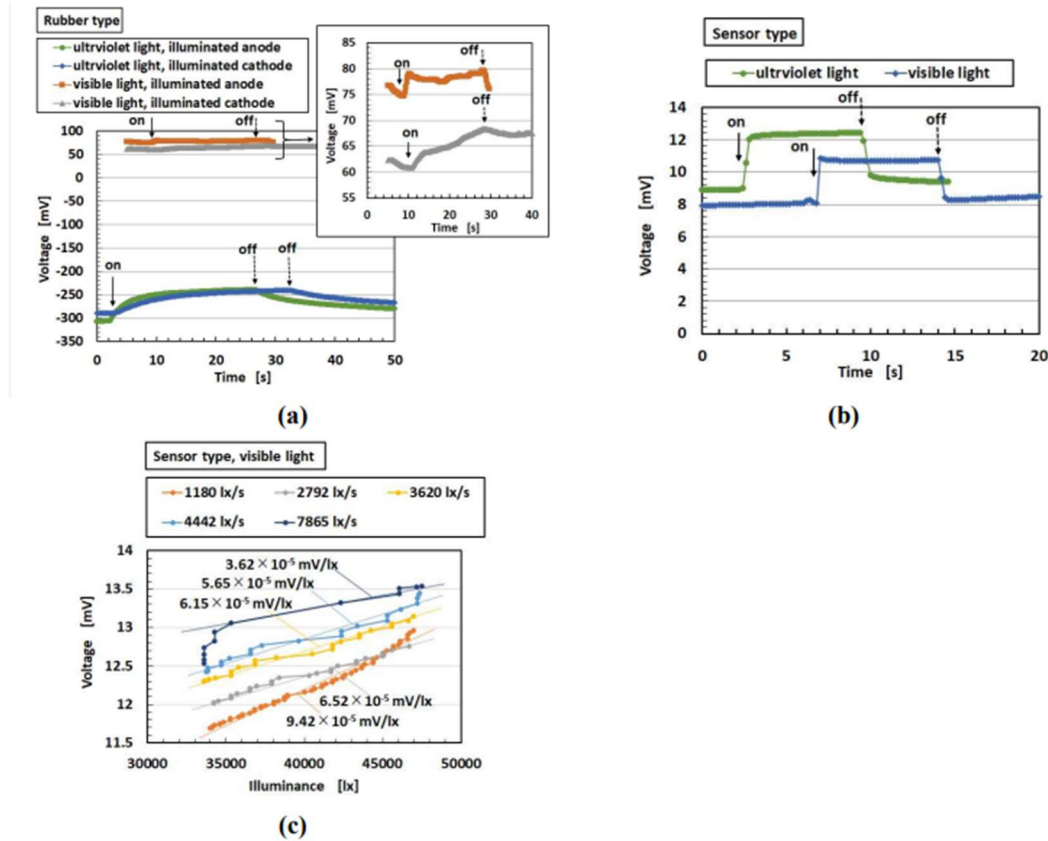


Figure 8. Reaction of the photovoltage to illumination: **(a)** electrolytically polymerized HF rubber type: illuminated on the anode side, as shown in **Figure 2b**; illuminated on the cathode side, as shown in **Figure 2d**; **(b)** optical biosensor; **(c)** the effect of illumination velocity in the case of the optical biosensor under visible light.

As seen from **Figure 8a**, the photovoltaic response is more sensitive to UV light than to visible light. The cause is due to the peculiarity of TiO_2 which is responsive to UV light, as being familiar in the field of solar cell. In addition, it is also conceivable that the double bond of the rubber such as CR and NR is responsive to UV light, as being also familiar in the field of rubber.

The intrinsic microscopic structure of electrolytically polymerized HF rubber, in which ionic polarization is dominant, is shown in Panels III–VI in **Figure 9**. The predominant molecules of rubber, water, particles of Fe_3O_4 , etc. are dopant D and acceptor A (**Figure 9**, Panel III), and are ionized respectively as D^+ and A^- (**Figure 9**, Panel IV). A^- is desorbed by holes (red dots in **Figure 9**). A^- and D^+ are static, and therefore create built-in voltage (**Figure 9**, Panel V). On the other hand, holes, electrons, and A^- to be absorbed with the electrons (yellow dots in **Figure 9**) are mobile, so they create built-in current (**Figure 9**, Panel V). Holes approach the negative area aggregated by A^- (to be desorbed by the hole), or A^- (to be absorbed by the electron) approaches the positive aggregated area of D^+ , and then the electrical double layer (EDL) is created (**Figure 9**, Panel VI). The chemical relation of D and A with S (which are molecules and particles contributing to the transfer of electric charge) brought about by illumination is shown in Equations (1) and (2) for the anode and cathode, respectively, which are the same as that in the case of DSSCs with MCF rubber [41].

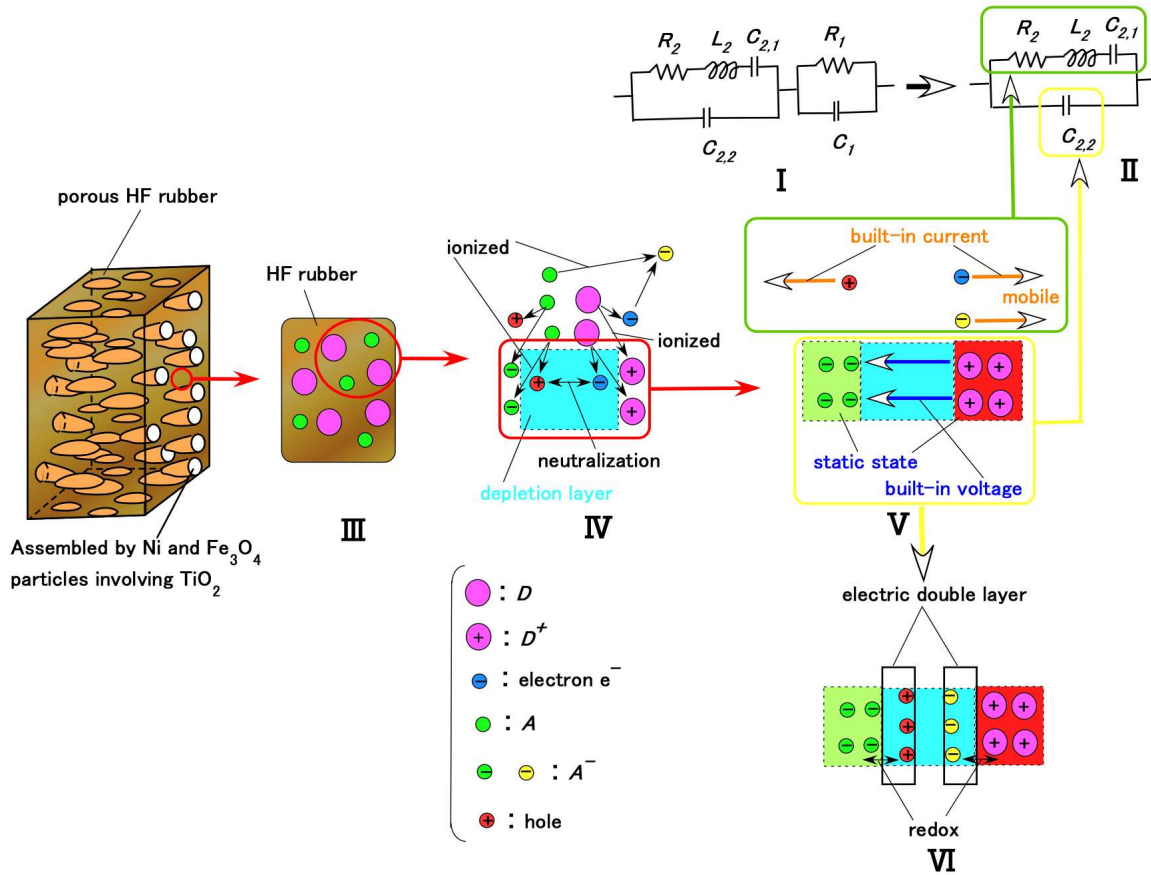
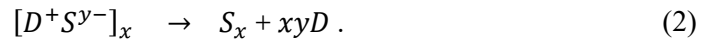
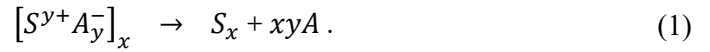


Figure 9. Physical model of the intrinsic structure and equivalent electric circuit of electrolytically polymerized HF rubber.

This reaction can occur under the outer-sphere electron transfer reaction (OSETR) according to the electron transfer theory of inorganic metal complexes, which states that the structural configuration of HF rubber does not allow deformation and only electrons are transferred [41]. This transfer occurs in two cases: one in which electrons transfer among molecules and particles where there is a small gap between them; and another in which electrons' jump is generated by the tunneling effect where there is a large gap between them.

The intrinsic structures with chemical reactions can be compared to the equivalent electric circuits of HF rubber (**Figure 9**, Panel I). Resistance R_1 and capacitance C_1 are very small between the electrode and the HF rubber, so the equivalent electric circuit of the HF rubber can be summarized as shown in Panel II of **Figure 9**. The integrated impedance of R_2 , L_2 , and $C_{2,1}$ is related to the built-in current corresponding to the bulk resistance (or charge transfer resistance) induced by ionic and electronic migration, which appear as ionic and electronic conductivity in the field of solid electrolytes. The $C_{2,2}$ capacitor is related to the built-in voltage inducing EDL capacitance, which is similar in appearance to solid electrolytes.

The response time t can be evaluated by the behavior of the electrons and ions (together known as the "carrier") induced from $C_{2,1}$, R_2 , L_2 , and $C_{2,2}$. In general, t is divided into three types, as shown in Equation (3): t_1 based on capacitance and resistance; t_2 based on the speed of carrier diffusion at deeper regions than the depletion layer; and t_3 based on the speed of carriers in the inner depletion layer.

$$t = \sqrt{t_1^2 + t_2^2 + t_3^2} \quad (3)$$

In the case of dominant behavior of the EDL (i.e., $C_{2,2}$), corresponding to the dominance of t_1 and t_3 (the velocity of carriers is large in the EDL), the response time is fast and the voltage under illumination can be represented as I in **Figure 9**. Therefore, the sensor type behaves as a dominant EDL under illumination. On the other hand, in the case of dominant behavior in an area outside the EDL (i.e., R_2 , L_2 , $C_{2,2}$), corresponding to the dominance of t_2 (the velocity of carriers is large in the region outside the EDL), the response time is slow and the voltage under illumination can be represented as II in **Figure 9**. Therefore, the rubber type behaves dominantly in the area outside the EDL under illumination.

Figure 8c shows the effect of the illumination velocity on photovoltage. As the illumination velocity increases, the gradient of change of the voltage slows. It means that the optical biosensor works faster according to the slow change of the illumination, which is typical results for the present optical biosensor.

3.2. CV profiles

In the case of the rubber type, as shown in **Figure 10a**, the CV profiles show a non-linear area between voltage V and electric current I , indicating that the oxidation-reduction reaction is large. The CV profiles correspond to the electrochemical behaviors of a pseudo-capacitor (PC). Profiles showing increasing voltage at plus current (A in **Figure A2** in Appendix) and decreasing voltage at minus current (D in **Figure A2**) indicate oxidation; on the other hand, those showing decreasing voltage at plus current (B in **Figure A2**) and increasing voltage at minus current (C in **Figure A2**) indicate reduction. In the case of the sensor type, the CV profiles are highly similar

to that of the EDL-capacitor (EDLC), whose PC profiles are linear between voltage and current (**Figure A2**). It is well known that the CV profile of an EDLC can be represented by a Butler-Volmer equation demonstrating the transfer of carriers under the assumption of both reactions at the anode and cathode, which create linear CV profiles. This is similar to the behavior of photodiodes.

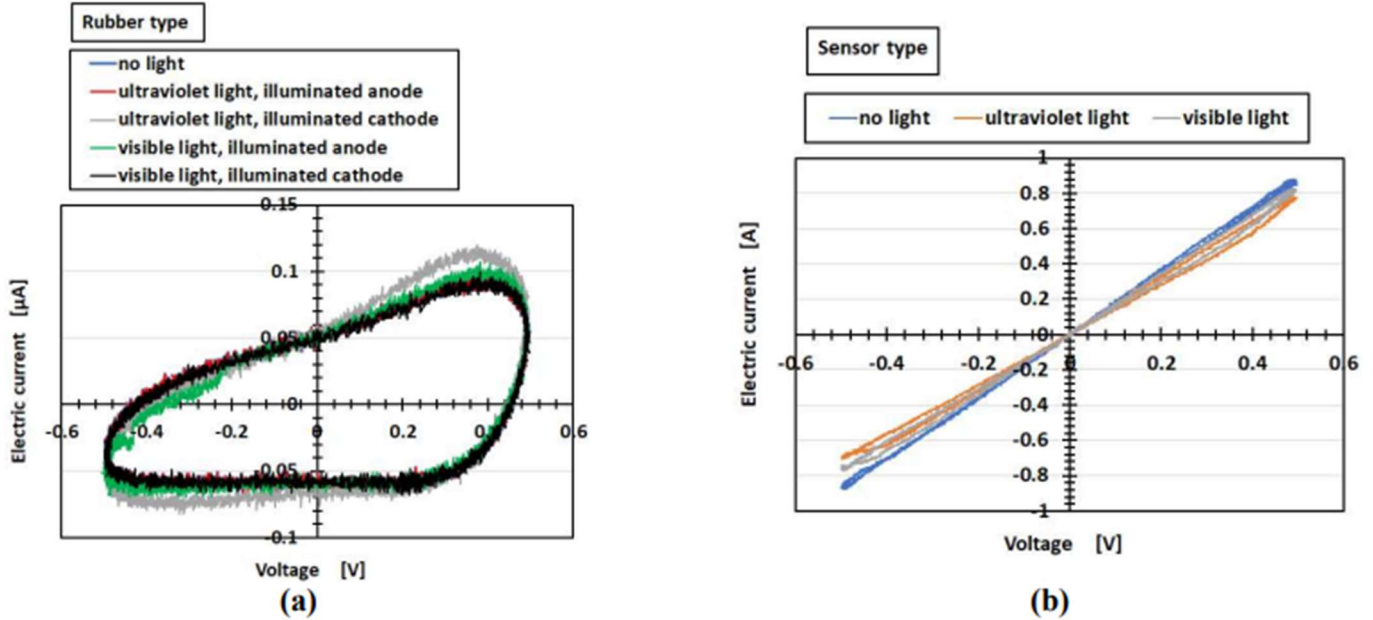


Figure 10. CV profiles: (a) electrolytically polymerized HF rubber type; (b) optical biosensor: no illumination (no light); illumination on the anode side of the HF rubber, as shown in **Figure 2b** (illuminated anode); illumination on the cathode side of the HF rubber, as shown in **Figure 2d** (illuminated cathode).

Note that the reaction of current to the voltage in the case of the rubber type is smaller than that with the sensor type. Therefore, the photovoltaic effect of the sensor type is larger than that of the rubber type.

Taken together with the above results, as shown in **Figure 11**, the relations among the photovoltaics and the CV profiles related to the equivalent electric circuit (depicted as II corresponding to Panel II in **Figure 9**) and the microscopic intrinsic structure (depicted as V corresponding to Panel V in **Figure 9**) can be demonstrated.

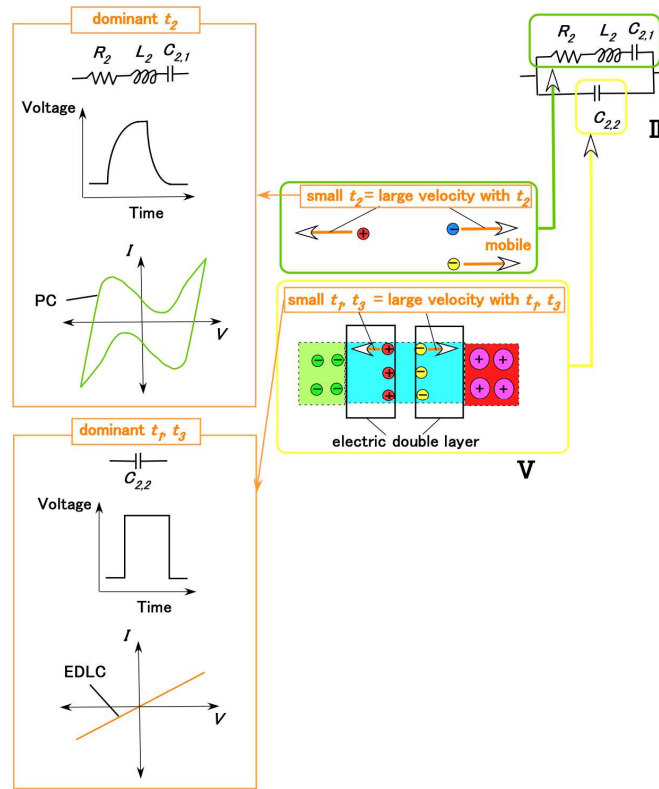


Figure 11. Relations among the photovoltaics, the CV profiles, the equivalent electric circuits, and the intrinsic microscopic structures.

In short, the HF optical biosensor has the electric circuit having dominant $C_{2,2}$ as shown by the Panel II in **Figure 9** and the dominant role of EDL in the HF material as shown by the Panel V in **Figure 11**. And then, the response time to the illumination becomes fast. These configurations of the electric circuit and the HF material are different from the ones in the rubber type as shown in **Figure 11**. The fast response is significant in the bio-mechanical applications such as artificial optical sensor like a retina in human eye ball. Therefore, the present HF optical biosensor is suitable for the bio-mechanical applications.

3.3. Electric properties

Next, we further investigate the relation between the intrinsic microscopic structure and the equivalent electric circuit, as shown in **Figures 9** and **11** in detail using EIS.

In the case of electrolytically polymerized HF rubber, as shown in **Figure 12**, the change in electric properties is divided into the A and B areas around the border of 10^4 frequency. At low frequencies, the current flows through $C_{2,1}$, R_2 , and L_2 more than through $C_{2,2}$, while at high frequencies, the current flows through $C_{2,2}$ more than through $C_{2,1}$, R_2 , or L_2 . Because absolute reactance X in area A (the low frequency region) is larger than that in area B (the high frequency region), as shown in **Figure 13b**, the current flows through $C_{2,1}$, R_2 , and L_2 more than through $C_{2,2}$. Therefore, the circuit part of $C_{2,1}$, R_2 , and L_2 is more dominant than that of $C_{2,2}$. Then, as shown in **Figure 11**, this situation corresponds to a dominant t_2 , a slow response of photovoltage

to illumination, and PC-CV profiles. This tendency does not change significantly with or without illumination.

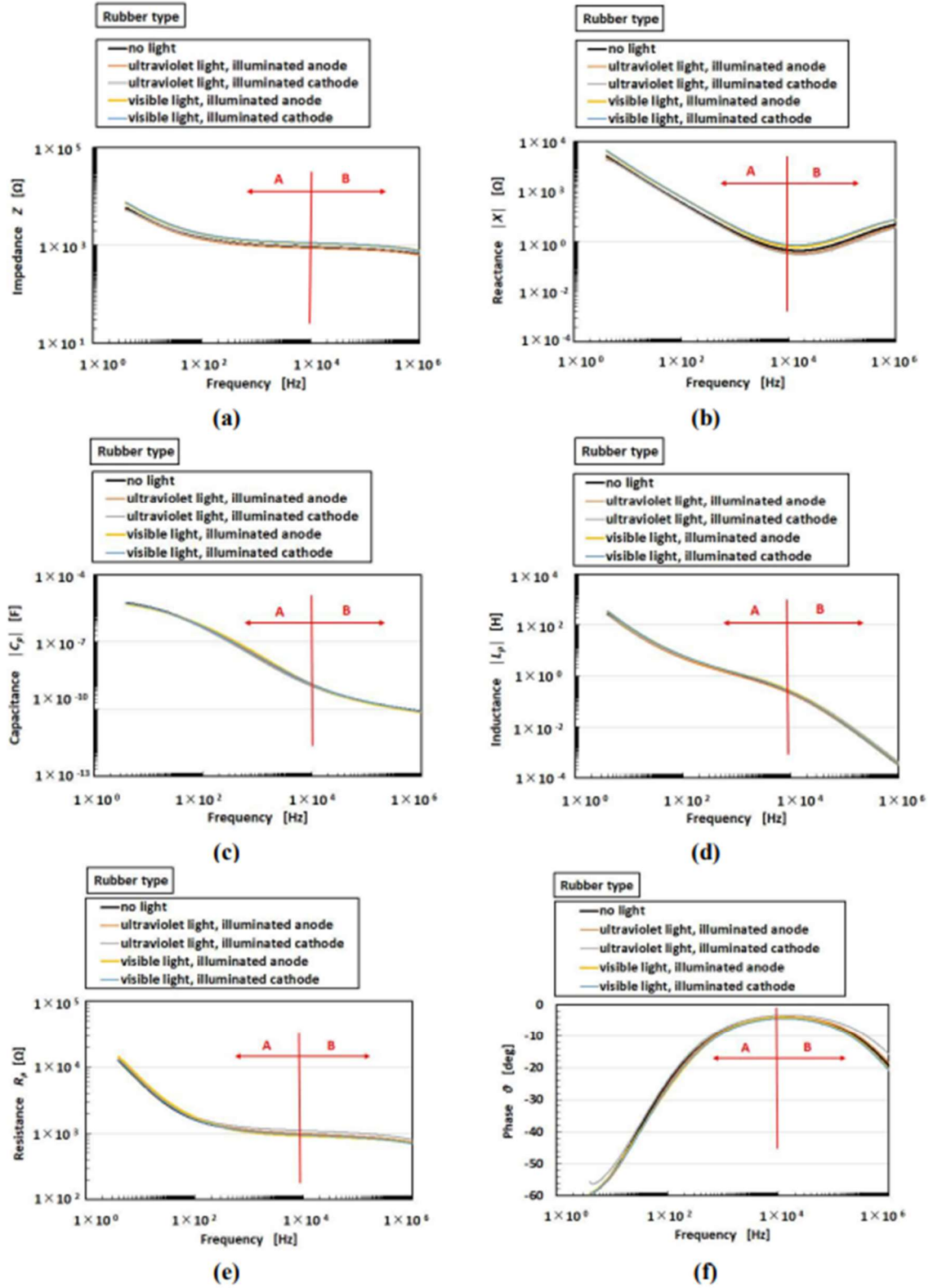


Figure 12. EIS results of electrolytically polymerized HF rubber: (a) impedance; (b) absolute value of reactance; (c) absolute value of capacitance; (d) absolute value of inductance; (e) resistance; (f) phase difference between voltage and electric current.

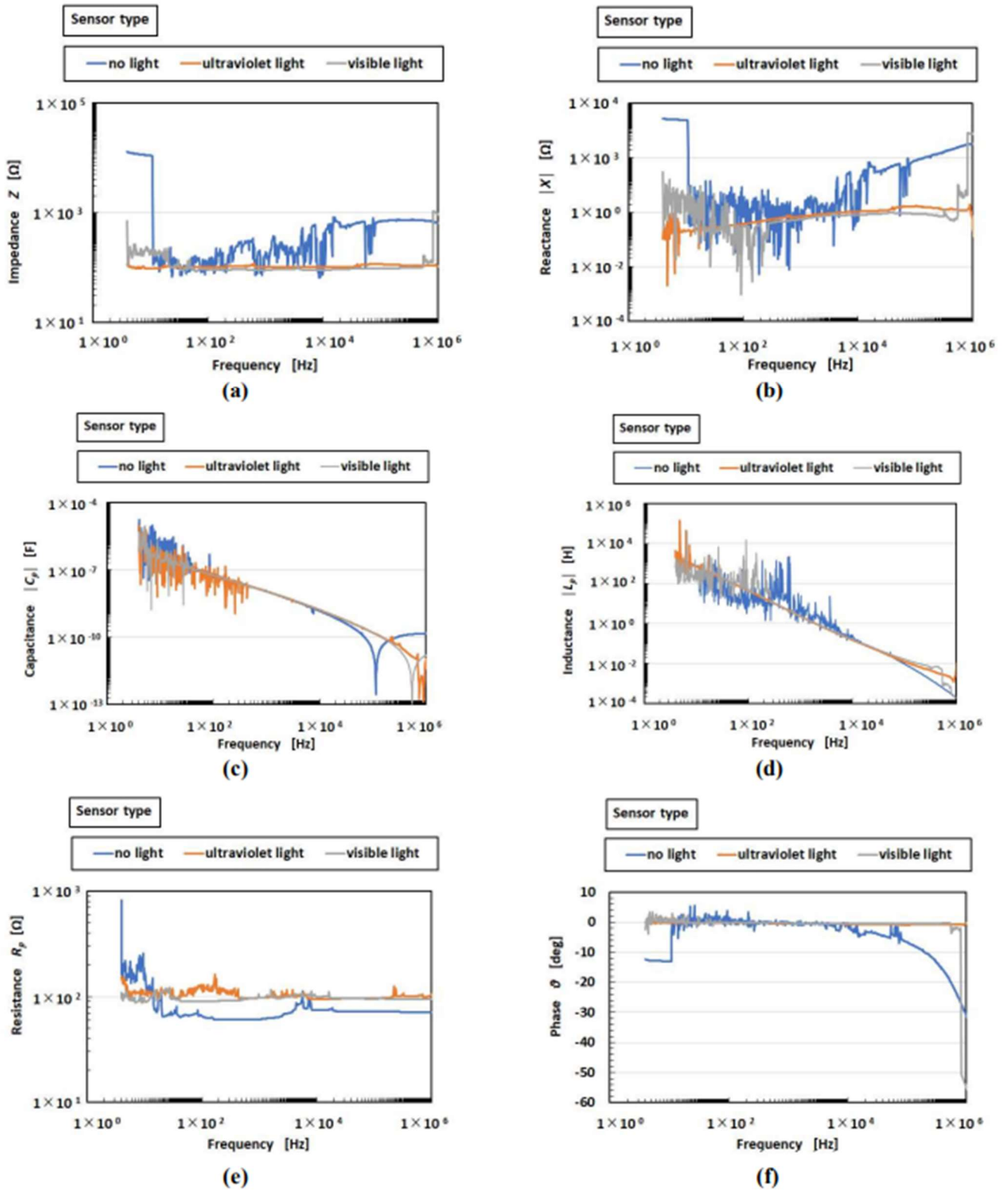


Figure 13. EIS results of the optical biosensor type: (a) impedance; (b) absolute value of reactance; (c) absolute value of capacitance; (d) absolute value of inductance; (e) resistance; (f) phase difference between voltage and electric current.

On the other hand, in the case of the optical biosensor type, as shown in **Figure 13**, the electric properties change with illumination. As shown in **Figures 13c–13e**, the effects of capacitance C_p and inductance L_p are larger than the effect of resistance R_p , whether by illumination or not. It is peculiar that phase q under illumination does not change by frequency (**Figure 13f**). This indicates that the equivalent circuit must be parallel. Absolute reactance X (**Figure 13b**) is shown in **Table 2**. The results show that, without illumination, the circuit part of $C_{2,1}$, R_2 , and L_2 is more dominant than that of $C_{2,2}$ because the absolute reactance X in the low-frequency region is larger than that in the high-frequency region. This tendency is the same as that in the case of the HF rubber type: t_2 is dominant (**Figure 11**). However, under illumination, the circuit part of $C_{2,2}$ is more dominant than that of $C_{2,1}$, R_2 , or L_2 because the absolute reactance X in the high-frequency region is larger than that in the low-frequency region. Therefore, it can be deduced that the photovoltaic effect is created by illumination dominantly at the inner EDL: t_1 and t_3 are dominant (**Figure 11**).

Table 2. Absolute value of reactance at low and high frequencies.

Illumination	Low frequency range [W] (at 4 Hz)	High frequency range [W] (at 8 GHz)
No light	2720	89.4
Visible light	31.2	84.2
UV light	0.107	83.3

3.4. Chemical-photovoltaic mechanism

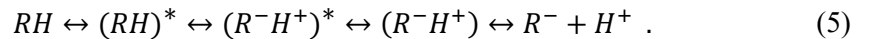
From a different perspective, the above relation between the intrinsic microscopic structure and the equivalent electric circuit can be verified by chemical reaction.

We can apply the chemical-photovoltaic reaction of DSSCs made with MCF rubber [41] to that of the present state-of-the-art optical biosensor. Here, for ease of understanding, we deal with the rubber molecules as polymers in order to focus on the monomer.

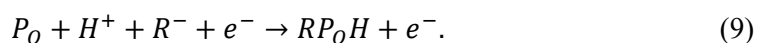
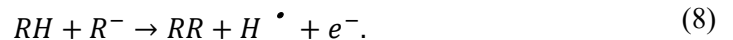
First, let us consider the isoprene molecule of the NR of MCF rubber. We define one unit of the isoprene molecule as RH presented as R , as shown in Equation (4).



Before we supply the electrolytic polymerization, RH is anionized to R^- , as shown in Equation (5), and the water molecules are ionized as shown in Equation (6). Then the generated radical OH^- becomes a hydroxyl radical $OH^\bullet$, as shown in Equation (7), due to certain influences such as unexpected experimental conditions.

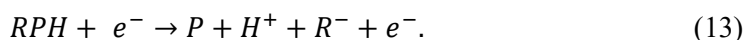
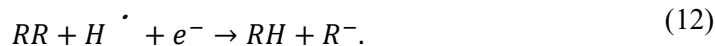


where electrolytic polymerization is applied, RR and RP_oH denote cross-linking created as shown in Equations (8) and (9), where P_o is the oleic acid coating around the Fe_3O_4 involved in MCF (Equation (10)) [41].

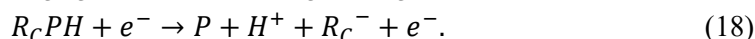




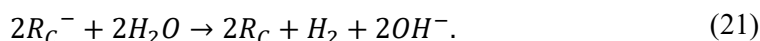
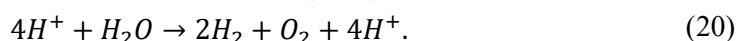
Next, regarding HF using NR, Equations (8) and (9) are also generated, replacing P_o with P as $C_{16}H_{33}NaO_4S$ molecule, as shown in Equation (11). Sequentially, under illumination, the reactions are reversely generated as shown in Equations (12) and (13). This reaction can occur under OSETR. H^+ creates the radical hydrogen $H^\bullet$, as shown in Equation (14), $H^\bullet$ generates the reaction as Equation (12), and the electron on the left side in Equation (14) transfers from the anode, as does that on the left side of Equation (12). The electron on the left side of Equation (13) transfers from the anode and that on the right transfers into the cathode. R^- on the right side of Equations (12) and (13) generates the reaction shown in Equation (15), and then the electron on the right side of Equation (15) transfers into the cathode.



The important key point of the cross-linking of NR is anionic isoprene molecule appearing as R^- . In the case of HF using CR, we see the same cross-linkings generated by electrolytic polymerization showing R_cR_c and R_cPH as those of RR and RPH , because of anionization on the unit of the chloroprene molecule as R_c in Equation (16): the electron in the R_c is biased owing to the chlorine of R_c so that R_c becomes R_c^- . Therefore, the cross-linking of CR is created by electrolytic polymerization. Under illumination, the reactions are generated sequentially as shown in Equations (14) and (17)–(19).



By the catalyst effect of TiO_2 , Ni , and Fe_3O_4 on HF using CR, H^+ , R^- and P^- are reacted, as shown in Equations (20)–(22). Here, P^- can easily be anionized as shown in Equation (23), and TiO_2 is created from $K_2TiO(C_2O_4)_2 \cdot 2H_2O$ solution shown below.

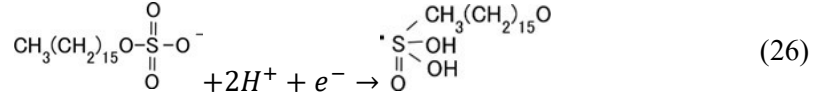
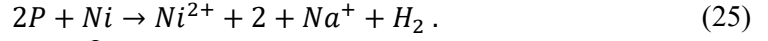


H^+ on the right side of Equation (20) creates $H^\bullet$ as shown in Equation (14). OH^- on the right side of Equations (21) and (22) creates $OH^\bullet$ as shown in Equation (7). $OH^\bullet$ is unstable enough to have a powerful oxidizing effect and therefore reacts with

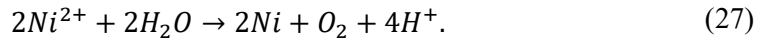
$H^\bullet$, as shown in Equation (24). The created H_2O is reacted again, as shown in Equations (6) and (20)–(22).



Additionally, upon electrolytic polymerization, $C_{16}H_{33}NaO_4S$ reacts with Ni, as shown in Equations (25) and (26).

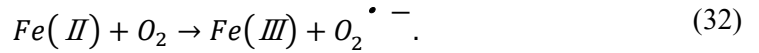
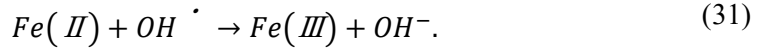
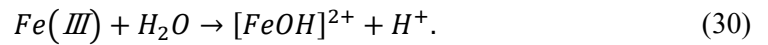
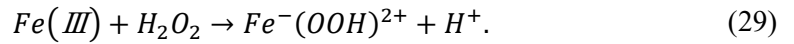
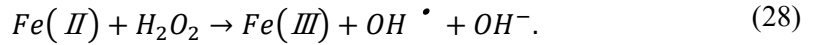


Ni^{2+} on the right side of Equation (25) is generated as shown in Equation (27) [42].



H^+ on the right side of Equation (27) creates Equation (14) and then Equation (24).

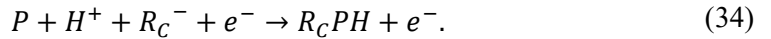
On the other hand, because Fe_3O_4 is structured with FeO and Fe_2O_3 , Fe_3O_4 is generated as shown in Equations (28)–(32), where $Fe(II)$ is FeO , $Fe(III)$ is Fe_2O_3 , and $O_2^{\bullet-}$ indicates superoxide radicals [43]. In particular, by the Fenton reaction, hydrogen peroxide H_2O_2 is reacted with $Fe(II)$.



Under illumination with UV light, $[FeOH]^{2+}$ in Equation (30) is generated as shown in Equation (33), and followed again by Equations (28)–(32).

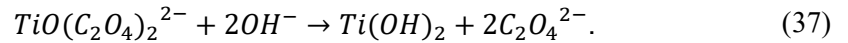
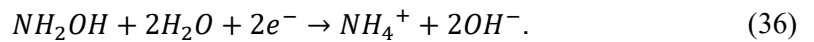
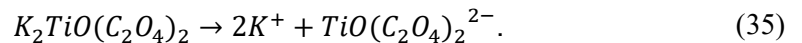


OH^- on the right side of Equations (28) and (31) creates Equation (24) through Equation (7); the electron on the right side of Equation (7) transfers into the anode. H^+ on the right side of Equations (29) and (30) creates Equations (34) and (14). The electron on the left side of Equation (34) transfers into the cathode.



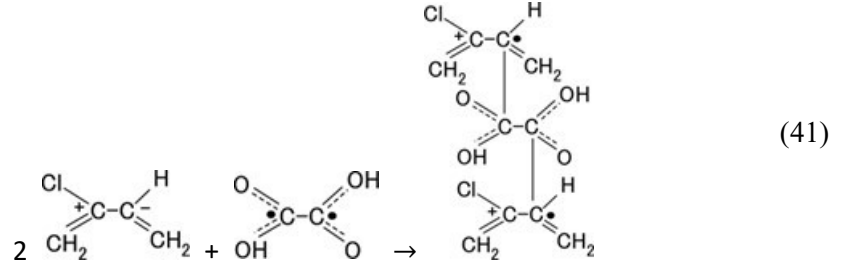
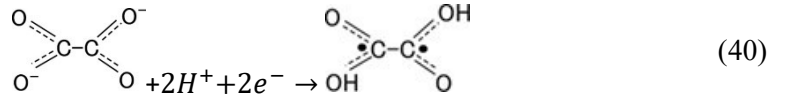
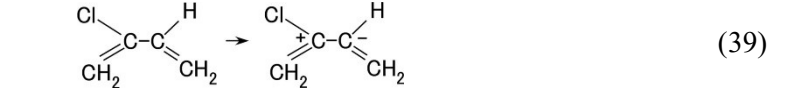
$H^\bullet$ generated by Equation (14) creates Equation (24); the electron on the left side of Equation (14) transfers from the cathode.

Next, we focus on TiO_2 . TiO_2 is created from $K_2TiO(C_2O_4)_2 \cdot 2H_2O$ solution, as shown in Equation (38) through Equations (35)–(37) [44].

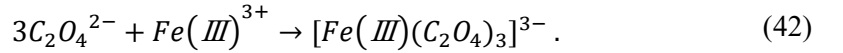


The oxalate ion $C_2O_4^{2-}$ in Equation (37) is reactive to rubber molecules such as NR and CR so that cross-linking between the anionic molecule of the rubber and

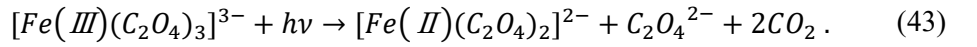
$C_2O_4^{2-}$ is created by electrolytic polymerization. Regarding HF rubber made by CR, cross-linking is created as shown in Equation (41) through Equations (39) and (40). Here, the electron in CR is biased by the chlorine, as shown in Equation (39).



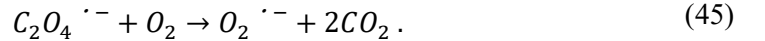
On the other hand, complex $Fe(III)(C_2O_4)_3^{3-}$ is created as shown in Equation (42).



Under illumination, $Fe(III)(C_2O_4)_3^{3-}$ absorbs the light so that Equations (43) and (44) are generated: the oxalate radical $C_2O_4^{\bullet-}$ is created.



$C_2O_4^{\bullet-}$ creates $O_2^{\bullet-}$, as shown in Equation (45).



H_2O_2 is also generated from $O_2^{\bullet-}$ by the transfer of the electron on the left side of Equation (46) from the anode. Equations (28) and (29) are then generated.



When the light is irradiated, the reactions below are generated by TiO_2 , which is created by Equation (38) [45–50]. First, hole h^+ and an electron are created from TiO_2 , as shown in Equation (47) [51].



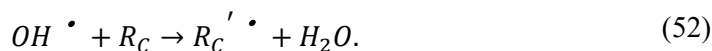
This electron on the right side of Equation (47) is scavenged by oxygen, and then $O_2^{\bullet-}$ is generated, as shown in Equation (48) [52,53].



Hole h^+ oxidizes chloroprene rubber molecules as shown in Equation (49), and reacts with water as shown in Equations (50) and (51).



$OH^\bullet$ in Equation (51) oxidizes R_c as shown in Equation (52), and reacts with $H^\bullet$ as shown in Equation (24). As a result, molecules of the rubber are oxidized, as shown in Equations (49) and (52) [54].



$O_2^{\bullet-}$ on the right side of Equation (48) is protonated, which means that proton H^+ is ionized, thereby generating hydroperoxyl radicals $HO_2^\bullet$, as shown in Equation (53).



H_2O_2 is generated as shown in Equation (54) from $HO_2^\bullet$ on the right side of Equation (53). Next, this H_2O_2 is reacted, as shown in Equations (28) and (29). Consequently, TiO_2 is reacted with Fe_3O_4 and water.



From $O_2^{\bullet-}$ in Equation (48), H_2O_2 is also generated, as shown in Equation (46).

3.5. Perspective of the optical biosensor

Finally, we show the concept as the feasibility of the production of the flexible and stretchable ophthalmologic biosensors mimicking the retina of the human eye. By utilizing many of our proposed optical biosensors as shown in **Figures 6c** and **6e**, we can produce an artificial eyeball (**Figure 14**). The artifact mimicking the vitreous body is a spherical gel wrapped by a membrane with a lens. The gel includes water in order to prevent the optical biosensors from drying, as shown in **Figure 6e**. The light enters the gel and is focused on the optical biosensors. The fabrication of this artificial eyeball and the experimental results will be discussed in a future article because of longer description to write.

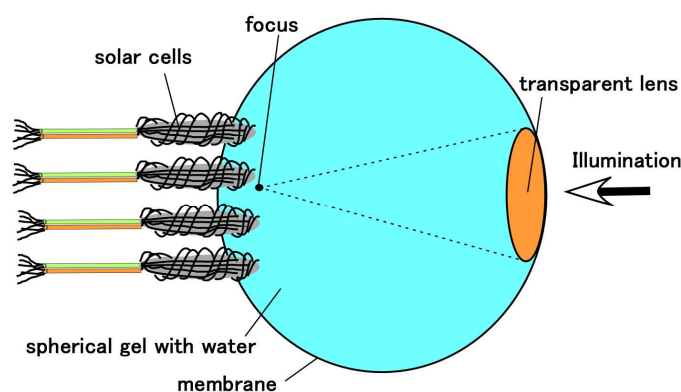


Figure 14. Schematic of an ophthalmological system utilizing HF rubber optical biosensors.

4. Conclusions

The physical paradigm of the fabrication and configuration of the solar cells develops the feasibility of the flexible and stretchable optical biosensors that mimic the human eye produced by the HF rubber. Therefore, in order to produce the TiO_2 layer involved in flexible and stretchable rubber or a coating on rubber, we propose a novel technique for producing photovoltaic material in which the rubber compounding

the TiO_2 metal complex is electrolytically polymerized. The creation of this solidified rubber involving TiO_2 is based on sequential chemical reactions, as shown in Equation (38).

In the case of using HF rubber, we obtain the photovoltage response to illumination with around 3–60 mV enhancement. And the HF optical biosensor has a fast response time to illumination of 0.4 ms, which is due to the electric circuit having dominant $C_{2,2}$ and the dominant role of EDL in the HF rubber. These configurations of the electric circuit and the HF material are different from the ones in the rubber type. Because the fast response is significant in bio-mechanical applications, the present HF optical biosensor is suitable for bio-mechanical applications such as artificial optical sensors like a retina in a human eyeball.

In addition, the experimental and physical paradigm of the electric and chemical properties and systems of the solar cells aid the photovoltaic structure of the optical biosensors, so that the characteristics, including the intrinsic structure of the optical biosensor, are elucidated as follows.

The electrolytically polymerized HF rubber type behaves dominantly in the area outside the EDL under illumination. Its behavior in the area outside the EDL (i.e., R_2 , L_2 , $C_{2,2}$) is dominant and the velocity of carriers is large in the region outside the EDL, as demonstrated by t_2 . The response time of photovoltage to illumination is slow. CV profiles show a non-linear area between voltage and current because the oxidation-reduction reaction is large. The CV profiles correspond to the electrochemical behaviors of PC.

On the other hand, the optical biosensor type behaves dominantly in the EDL (i.e., $C_{2,2}$) under illumination. The velocity of carriers is large in the EDL, as demonstrated by t_1 and t_3 . The response time is fast. CV profiles are highly similar to that of the EDLC, whose PC profiles are linear between voltage and current. It is also similar to the behavior of photodiodes.

In addition, these results on the intrinsic microscopic structure by R , C , and L can be verified by the electric properties obtained by EIS measurement.

In particular, the highlighted consequence is as follows:

- 1) The flexible and stretchable optical biosensor without having solid transparent glass can be produced with using $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ solution by electrolytic polymerization.
- 2) The photovoltage response to illumination of the optical sensor has around 3–60 mV enhancement.

The findings obtained in the present study on the production of TiO_2 on rubber are useful for the production of other materials coated with or involving TiO_2 . Other semiconductors, such as ZnO and SnO, might be expected to be effective for the production of the photovoltaic layer in electrolytically polymerized rubber. And then, the photovoltaic effect might result in an enhancement in the illumination of visible light. Therefore, the development of a novel fabrication technique for the optical biosensor would lead to many advances, as would the fabrication of ophthalmological systems mimicking the human eyeball. In addition to optical sensing, if we can reproduce the tactile, gustatory, olfactory, auditory, and equilibrium sensations through the use of artifacts utilizing MCF or HF rubber, the five senses could be produced in a bio-inspired humanoid robot.

At last, as shown in **Figure 7b**, the adhesion technique of the outer thin electric wires on the surface of the rubber coating with TiO_2 by using any other rubbers is the only remaining engineering problem. In the present study, the outer thin electric wires are wound around the rubber, as shown in **Figure 1b**. This is the future work to be conducted on the consummated production of the rubber-made solar cell. We are trying the study currently, and then the findings will be presented in another article.

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Conflict of interest: The author declares no conflict of interest.

References

1. Yang GZ, Bellingham J, Dupont PE, et al. The grand challenges of Science Robotics. *Science Robotics*. 2018, 3(14). doi: 10.1126/scirobotics.aar7650
2. Mehrali M, Bagherifard S, Akbari M, et al. Blending Electronics with the Human Body: A Pathway toward a Cybernetic Future. *Advanced Science*. 2018, 5(10). doi: 10.1002/advs.201700931
3. Yu H, Li H, Sun X, et al. Biomimetic Flexible Sensors and Their Applications in Human Health Detection. *Biomimetics*. 2023, 8(3): 293. doi: 10.3390/biomimetics8030293
4. Heng W, Solomon S, Gao W. Flexible Electronics and Devices as Human–Machine Interfaces for Medical Robotics. *Advanced Materials*. 2022, 34(16). doi: 10.1002/adma.202107902
5. Luan H, Zhang Y. Programmable Stimulation and Actuation in Flexible and Stretchable Electronics. *Advanced Intelligent Systems*. 2021, 3(6). doi: 10.1002/aisy.202000228
6. Chadha U, Bhardwaj P, Agarwal R, et al. Recent progress and growth in biosensors technology: A critical review. *Journal of Industrial and Engineering Chemistry*. 2022, 109: 21-51. doi: 10.1016/j.jiec.2022.02.010
7. Chortos A, Liu J, Bao Z. Pursuing prosthetic electronic skin. *Nature Materials*. 2016, 15(9): 937-950. doi: 10.1038/nmat4671
8. Yang JC, Mun J, Kwon SY, et al. Electronic Skin: Recent Progress and Future Prospects for Skin-Attachable Devices for Health Monitoring, Robotics, and Prosthetics. *Advanced Materials*. 2019, 31(48). doi: 10.1002/adma.201904765
9. Zhang N, Wei X, Fan Y, et al. Recent advances in development of biosensors for taste-related analyses. *TrAC Trends Anal. Chem.* 2020, 129: 115925.
10. Covington JA, Marco S, Persaud KC, et al. Artificial Olfaction in the 21st Century. *IEEE Sensors Journal*. 2021, 21(11): 12969-12990. doi: 10.1109/jsen.2021.3076412
11. Guo H, Pu X, Chen J, et al. A highly sensitive, self-powered triboelectric auditory sensor for social robotics and hearing aids. *Science Robotics*. 2018, 3(20). doi: 10.1126/scirobotics.aat2516
12. Vikas V, Crane C. Bioinspired dynamic inclination measurement using inertial sensors. *Bioinspiration & Biomimetics*. 2015, 10(3): 036003. doi: 10.1088/1748-3190/10/3/036003
13. Shimada K. Morphological Configuration of Sensory Biomedical Receptors Based on Structures Integrated by Electric Circuits and Utilizing Magnetic-Responsive Hybrid Fluid (HF). *Sensors*. 2022, 22(24): 9952. doi: 10.3390/s22249952
14. Shim J, Park H, Kang D, et al. Electronic and Optoelectronic Devices based on Two-Dimensional Materials: From Fabrication to Application. *Advanced Electronic Materials*. 2017, 3(4). doi: 10.1002/aelm.201600364
15. Wang X, Cui Y, Li T, et al. Recent Advances in the Functional 2D Photonic and Optoelectronic Devices. *Advanced Optical Materials*. 2018, 7(3). doi: 10.1002/adom.201801274
16. Bao X, Ou Q, Xu Z, et al. Band Structure Engineering in 2D Materials for Optoelectronic Applications. *Advanced Materials Technologies*. 2018, 3(11). doi: 10.1002/admt.201800072
17. Kim, T. Y.; Suh, W.; Jeong, U. Approaches to deformable physical sensors: Electronic versus iontronic. *Mat. Sci. Eng. R* 2021, 146, 100640.

18. Chen Q, De Marco N, Yang Y, et al. Under the spotlight: The organic–inorganic hybrid halide perovskite for optoelectronic applications. *Nano Today*. 2015, 10(3): 355-396. doi: 10.1016/j.nantod.2015.04.009
19. Kovalenko MV, Protesescu L, Bodnarchuk MI. Properties and potential optoelectronic applications of lead halide perovskite nanocrystals. *Science*. 2017, 358(6364): 745-750. doi: 10.1126/science.aam7093
20. Long G, Sabatini R, Saidaminov MI, et al. Chiral-perovskite optoelectronics. *Nature Reviews Materials*. 2020, 5(6): 423-439. doi: 10.1038/s41578-020-0181-5
21. Kang P, Wang MC, Knapp PM, et al. Crumpled Graphene Photodetector with Enhanced, Strain-Tunable, and Wavelength-Selective Photoresponsivity. *Advanced Materials*. 2016, 28(23): 4639-4645. doi: 10.1002/adma.201600482
22. Ko S, Mondal R, Risko C, et al. Tuning the Optoelectronic Properties of Vinylene-Linked Donor–Acceptor Copolymers for Organic Photovoltaics. *Macromolecules*. 2010, 43(16): 6685-6698. doi: 10.1021/ma101088f
23. Ullbrich S, Benduhn J, Jia X, et al. Emissive and charge-generating donor–acceptor interfaces for organic optoelectronics with low voltage losses. *Nature Materials*. 2019, 18(5): 459-464. doi: 10.1038/s41563-019-0324-5
24. Svechtarova MI, Buzzacchera I, Toebes BJ, et al. Sensor Devices Inspired by the Five Senses: A Review. *Electroanalysis*. 2016, 28(6): 1201-1241. doi: 10.1002/elan.201600047
25. Ji X, Zhao X, Tan MC, et al. Artificial Perception Built on Memristive System: Visual, Auditory, and Tactile Sensations. *Advanced Intelligent Systems*. 2020, 2(3). doi: 10.1002/aisy.201900118
26. Bao R, Wang C, Dong L, et al. Flexible and Controllable Piezo-Phototronic Pressure Mapping Sensor Matrix by ZnO NW/p-Polymer LED Array. *Advanced Functional Materials*. 2015, 25(19): 2884-2891. doi: 10.1002/adfm.201500801
27. Jung YH, Park B, Kim JU, et al. Bioinspired Electronics for Artificial Sensory Systems. *Advanced Materials*. 2018, 31(34). doi: 10.1002/adma.201803637
28. Khan F, Khan MT, Rehman S, et al. Analysis of electrical parameters of p-i-n perovskites solar cells during passivation via N-doped graphene quantum dots. *Surfaces and Interfaces*. 2022, 31: 102066. doi: 10.1016/j.surf.2022.102066
29. Zhang L, Mei L, Wang K, et al. Advances in the Application of Perovskite Materials. *Nano-Micro Letters*. 2023, 15(1). doi: 10.1007/s40820-023-01140-3
30. Maulida PYD, Subagyo R, Hartati S, et al. Recent progress and rational design of perovskite-based chemosensors: A review. *Journal of Alloys and Compounds*. 2023, 962: 170996. doi: 10.1016/j.jallcom.2023.170996
31. Vinoth S, Kanimozhi G, Narsimulu D, et al. Ionic relaxation of electrospun nanocomposite polymer-blend quasi-solid electrolyte for high photovoltaic performance of Dye-sensitized solar cells. *Materials Chemistry and Physics*. 2020, 250: 122945. doi: 10.1016/j.matchemphys.2020.122945
32. Tapa AR, Xiang W, Zhao X. Metal Chalcogenides (MxEy, E = S, Se, and Te) as Counter Electrodes for Dye–Sensitized Solar Cells: An Overview and Guidelines. *Advanced Energy and Sustainability Research*. 2021, 2(10). doi: 10.1002/aesr.202100056
33. Fegade U, Conghao C, Chen YJ, et al. Comparative analysis of the photovoltaic cell parameters of dye-sensitized solar cells with composite photoanodes: Effect of the alien component. *Optical Materials*. 2023, 143: 114109. doi: 10.1016/j.optmat.2023.114109
34. He X, Duan F, Liu J, et al. Transparent Electrode Based on Silver Nanowires and Polyimide for Film Heater and Flexible Solar Cell. *Materials*. 2017, 10(12): 1362. doi: 10.3390/ma10121362
35. Peng M, Dong B, Zou D. Three dimensional photovoltaic fibers for wearable energy harvesting and conversion. *Journal of Energy Chemistry*. 2018, 27(3): 611-621. doi: 10.1016/j.jechem.2018.01.008
36. Zhang H, Zhu X, Tai Y, et al. Recent advances in nanofiber-based flexible transparent electrodes. *International Journal of Extreme Manufacturing*. 2023, 5(3): 032005. doi: 10.1088/2631-7990/acdc66
37. Bai H, Li S, Barreiros J, et al. Stretchable distributed fiber-optic sensors. *Science*. 2020, 370(6518): 848-852. doi: 10.1126/science.aba5504
38. Li W, Ke K, Jia J, et al. Recent Advances in Multiresponsive Flexible Sensors towards E-skin: A Delicate Design for Versatile Sensing. *Small*. 2021, 18(7). doi: 10.1002/smll.202103734
39. Prestopino G, Orsini A, Baretin D, et al. Vertically Aligned Nanowires and Quantum Dots: Promises and Results in Light Energy Harvesting. *Materials*. 2023, 16(12): 4297. doi: 10.3390/ma16124297
40. Shimada K, Ikeda R, Kikura H, et al. Morphological Fabrication of Rubber Cutaneous Receptors Embedded in a Stretchable Skin-Mimicking Human Tissue by the Utilization of Hybrid Fluid. *Sensors*. 2021, 21(20): 6834. doi: 10.3390/s21206834

41. Shimada K, Kikura H, Ikeda R, et al. Clarification of Catalytic Effect on Large Stretchable and Compressible Rubber Dye-Sensitized Solar Cells. *Energies*. 2020, 13(24): 6658. doi: 10.3390/en13246658
42. Iwasawa, Y. Tailored Metal Catalysts; D. Reidel Publishing Company; 1986. pp. 167-172.
43. Durán A, Monteagudo JM, San Martín I. Operation costs of the solar photo-catalytic degradation of pharmaceuticals in water: A mini-review. *Chemosphere*. 2018, 211: 482-488. doi: 10.1016/j.chemosphere.2018.07.170
44. Ishizaki H, Yokokawa Y, Matsumoto T, et al. New low-deposition technology for formation of titanium dioxide films. *J. Facul. Eng., Saitama Insti. Tech.* 2016, 26: 29-34.
45. Sun H, Bai Y, Jin W, et al. Visible-light-driven TiO₂ catalysts doped with low-concentration nitrogen species. *Solar Energy Materials and Solar Cells*. 2008, 92(1): 76-83. doi: 10.1016/j.solmat.2007.09.003
46. Ito S, Nazeeruddin MK, Zakeeruddin SM, et al. Study of Dye-Sensitized Solar Cells by Scanning Electron Micrograph Observation and Thickness Optimization of Porous TiO₂ Electrodes. *International Journal of Photoenergy*. 2009, 2009: 1-8. doi: 10.1155/2009/517609
47. Ilyas AM, Gondal MA, Baig U, et al. Photovoltaic performance and photocatalytic activity of facile synthesized graphene decorated TiO₂ monohybrid using nanosecond pulsed ablation in liquid technique. *Solar Energy*. 2016, 137: 246-255. doi: 10.1016/j.solener.2016.08.019
48. Lu WH, Chou CS, Chen CY, et al. Preparation of Zr-doped mesoporous TiO₂ particles and their applications in the novel working electrode of a dye-sensitized solar cell. *Advanced Powder Technology*. 2017, 28(9): 2186-2197. doi: 10.1016/j.appt.2017.05.026
49. Shamsudin NH, Shafie S, Ab Kadir MZA, et al. Power conversion efficiency (PCE) performance of back-illuminated DSSCs with different Pt catalyst contents at the optimized TiO₂ thickness. *Optik*. 2020, 203: 163567. doi: 10.1016/j.ijleo.2019.163567
50. El Haimeur A, Makha M, Bakkali H, et al. Enhanced performance of planar perovskite solar cells using dip-coated TiO₂ as electron transporting layer. *Solar Energy*. 2020, 195: 475-482. doi: 10.1016/j.solener.2019.11.094
51. Abdel-Maksoud YK, Imam E, Ramadan AR. TiO₂ water-bell photoreactor for wastewater treatment. *Solar Energy*. 2018, 170: 323-335. doi: 10.1016/j.solener.2018.05.053
52. Qin G, Wu Q, Sun Z, et al. Enhanced photoelectrocatalytic degradation of phenols with bifunctionalized dye-sensitized TiO₂ film. *Journal of Hazardous Materials*. 2012, 199-200: 226-232. doi: 10.1016/j.jhazmat.2011.10.092
53. Monteagudo JM, Durán A, Chatzisyneon E, et al. Solar activation of TiO₂ intensified with graphene for degradation of Bisphenol-A in water. *Solar Energy*. 2018, 174: 1035-1043. doi: 10.1016/j.solener.2018.09.084
54. Etacheri V, Di Valentin C, Schneider J, et al. Visible-light activation of TiO₂ photocatalysts: Advances in theory and experiments. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*. 2015, 25: 1-29. doi: 10.1016/j.jphotochemrev.2015.08.003

Appendix

Schematic profiles of experimental results on the curve of voltage responsive to the illumination are shown in **Figure A1**, and those of CV relations in **Figure A2**.

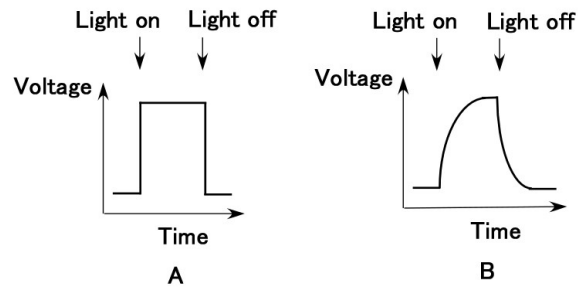


Figure A1. Schematic response curve of voltage with lights turned on and off.

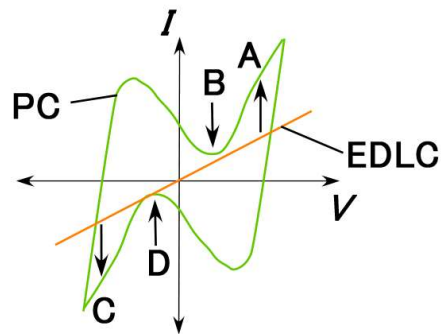


Figure A2. Schematic CV profiles of PC and EDLC.