

Response of biophotonic device using retinoid

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The authors focus on the retina in the human eye and consider retinoic acid to be the most appropriate for use in photoreceptive devices. The authors fabricated retinoic acid–chitosan film by using the layer-by-layer self-assembly process. The photocurrent value of the devices increased from 4.0 to 7.0 mA when used in optimized conditions. One of the best responses of these manually fabricated photoreceptive devices was that the photocurrent was 7 mA and the photocurrent response continued during the longest period to date of 9 h, which is an 81 times longer life time than before. The authors calculated the external quantum efficiency of the photocurrent response for devices with the best performance. The estimated external quantum efficiency of the photocurrent response for the best device was 4.53. In comparison, for one of the gel-type devices, the efficiency was 0.004. The mechanism of the photocurrent response of biophotonic devices seems to be the radical reaction rather than any ionic or charged carrier reaction.

1. Introduction

The rhodopsin in the human eye can convert photons into highly sensitive electrical signals by using ultrahigh-speed photoisomerization.¹ Although devices based on biological molecules have a limited lifetime and a low environmental resistance and stability, they also have superior functions, such as the ability to self-repair and self-organize.^{2,3} In this study, the authors focus on the retina in the human eye to fabricate a biophotonic device with biomimetic functions.^{4,5} The authors analyzed the photoisomerization reaction of the retinoids (retinal, retinoic acid (RA) and retinol) by using nuclear magnetic resonance (NMR) spectroscopy and observed that these retinoids were photoisomerized into three new isomers through radical reactions.⁴ The results from a Windows Molecular Orbital Package (WinMOPAC) analysis showed that RA had the lowest highest unoccupied molecular orbital (HOMO) energy level,⁵ and therefore, considered it to be the most appropriate for use in photoreceptive devices. The authors also reported that the fabrication conditions could be optimized by using a layer-by-layer self-assembly (LBL-SA) process.⁴ The external quantum

efficiency of the photocurrent response of biophotonic devices that use retinoids is reported in this article.

2. Analysis of photoisomerization reaction of retinoids

The authors have already reported the analysis results from the photoisomerization reaction of retinoids.⁴ If UV light is irradiated onto biophotonic devices made from retinal, the retinal molecules photoisomerize (Figure 1) and generate hydrogen and retinal radicals.

The authors have analyzed the photoisomerization reaction of some of the retinoids (retinal, RA and retinol) using NMR and estimated that these retinoids have photoisomerized into three new isomers through radical reactions.

The mechanism for the photocurrent response of biophotonic devices made from RA is shown in Figure 2. Light illumination generates the hydrogen and RA radicals. The RA radicals terminate

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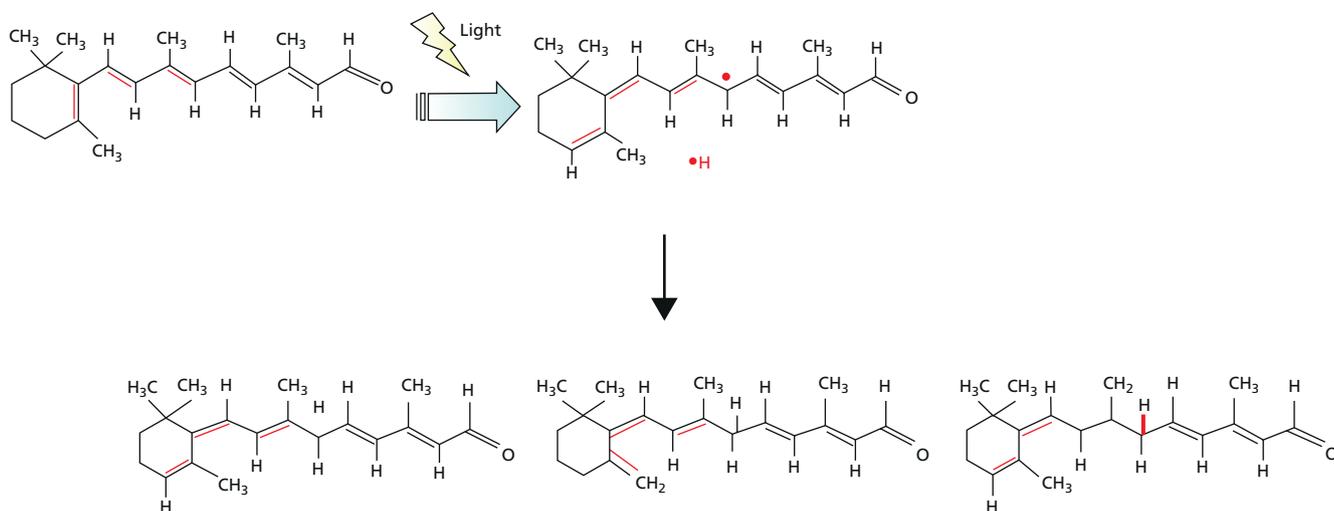


Figure 1. Photoisomerization reaction of all-trans retinal

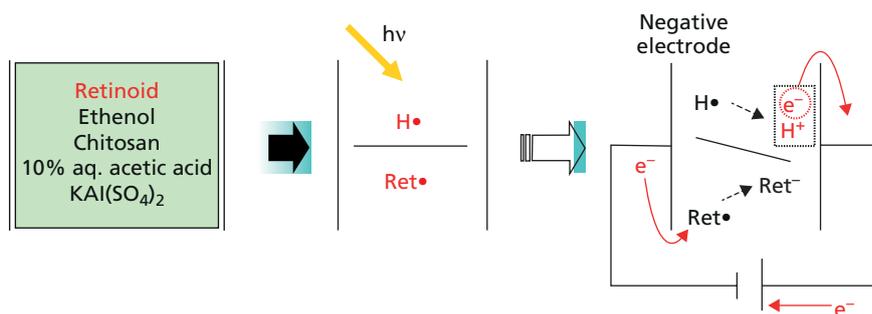


Figure 2. Mechanism for photocurrent response of biophotonic devices

Structure	Dipole moment: Debye	HOMO energy level: eV	LUMO energy level: eV	Bandgap energy: eV	Absorption wavelength: nm	Stability order
All-trans retinal	4.687	-8.3937	-0.9433	7.4504	352.54	Second
All-trans retinoic acid	6.527	-8.5005	-1.0253	7.4752	340.56	First
All-trans retinol	2.204	-8.1375	-0.5242	7.6133	324.49	Third

HOMO, highest occupied molecular orbital; LUMO, lowest unoccupied molecular orbital.

Table 1. Analytical results of retinoid molecules using Windows Molecular Orbital Package

by accepting electrons from a negative electrode and then change into a RA anion. The hydrogen radicals also terminate after donating electrons to the positive electrode and change into a H^+ ion. The RA anions and H^+ ions recombine and offer repeated responses to the illuminating light.

The results from the WinMOPAC analysis also showed that both the HOMO and lowest unoccupied molecular orbital energy levels of RA are the lowest, as listed in Table 1.⁵ Therefore, the authors believe RA is the most appropriate for use in photoreceptive devices.

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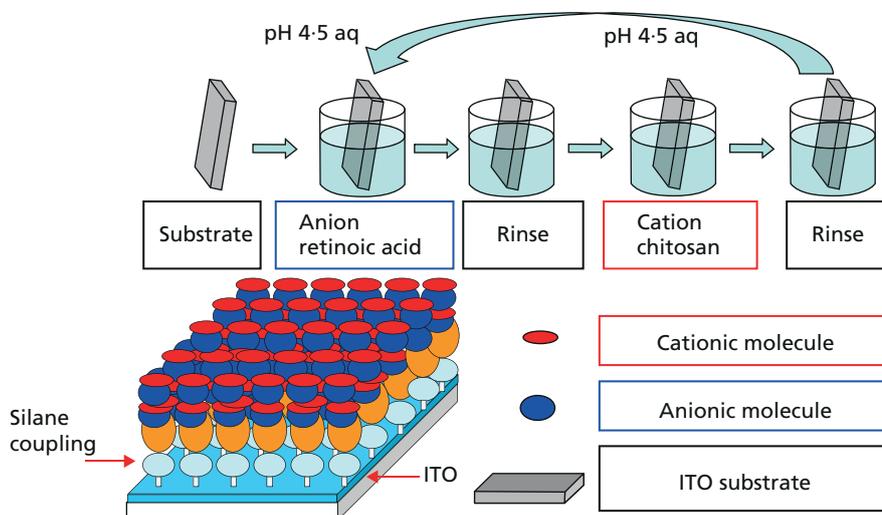


Figure 3. Retinoic acid-chitosan self-assembled film fabrication process

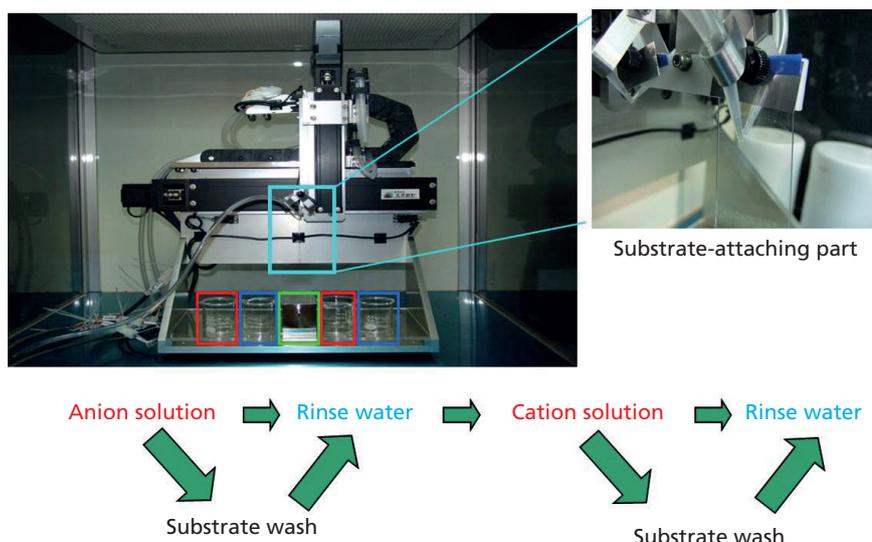


Figure 4. Automatic layer-by-layer self-assembling machine

3. Experiments

The authors fabricated RA-chitosan film using the LBL-SA process shown in Figure 3. A film of indium tin oxide on a glass substrate was treated with a silane-coupling reagent of 3-amino-propyl-tri-ethoxy silane. The authors immersed this film in an anionic solution for 20 min (all-trans RA solution, potential hydrogen (pH) 4-5), rinsed the film in pure water for 10 min, immersed it in a cationic solution for 20 min (chitosan solution, pH 4-5) and then rinsed in pure water for 10 min. These steps were repeated in the cyclic fashion shown in Figure 3.

These processes were automated and also fabricated RA-chitosan films using the automatic layer-by-layer self-assembly machine shown in Figure 4.

The authors fabricated gel-type film by using a RA-chitosan solution mixture to use as a comparison.⁵ Twelve and a half milligram solution of all-trans retinal were dissolved in 25 ml of ethanol, and 500 mg of chitosan and 50 mg of potassium alum were dissolved in 50 ml of 10% acetic acid. These solutions were mixed to form a retinal-chitosan sol solution. Then, 0.2 ml of this sol solution was sandwiched between two pieces of indium tin oxide-coated glass.

The authors then sandwiched the self-assembled film between a gold-plate and an indium tin oxide slide glass. After that, the devices were irradiated with a 365-nm light at 20-s intervals, and the photocurrent generation was measured by using an auto shutter-controlled digital multimeter; the data were sent to a computer, as shown in Figure 5.

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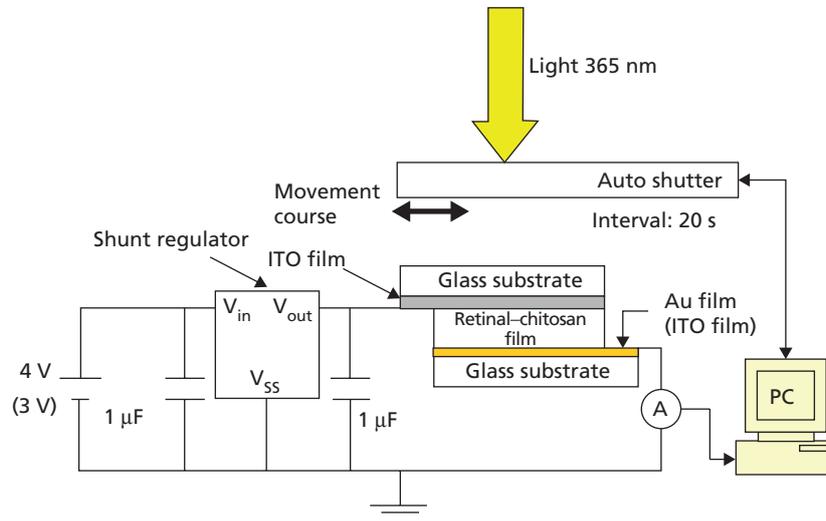


Figure 5. Photocurrent-response measurement system

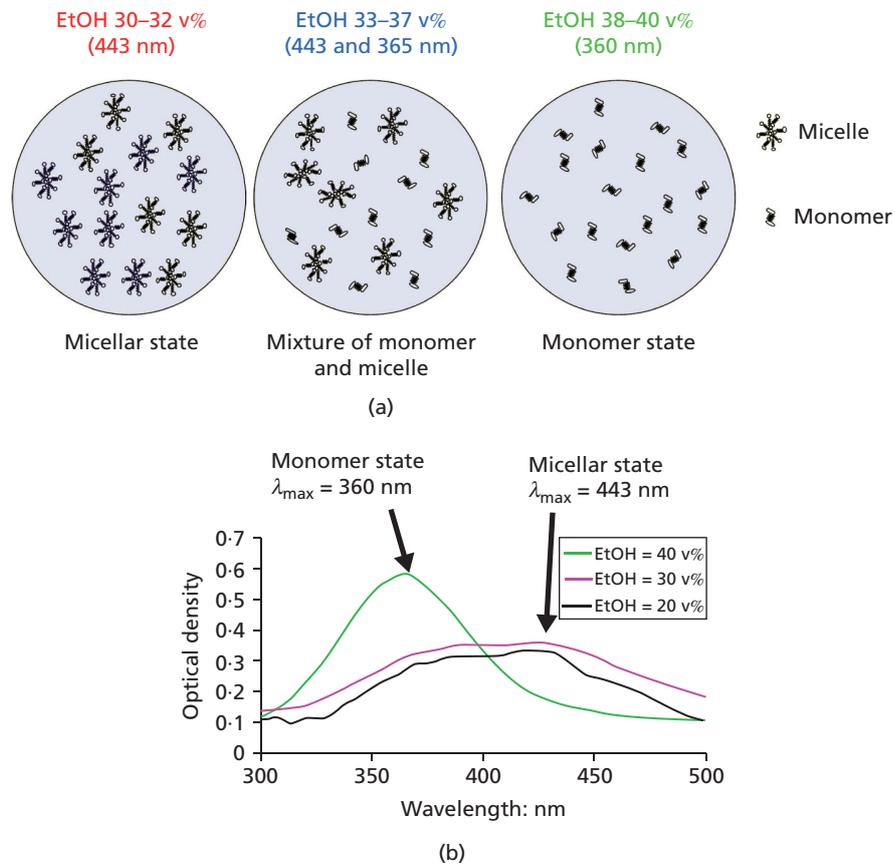


Figure 6. Association state in each solution condition and corresponding each absorption spectra

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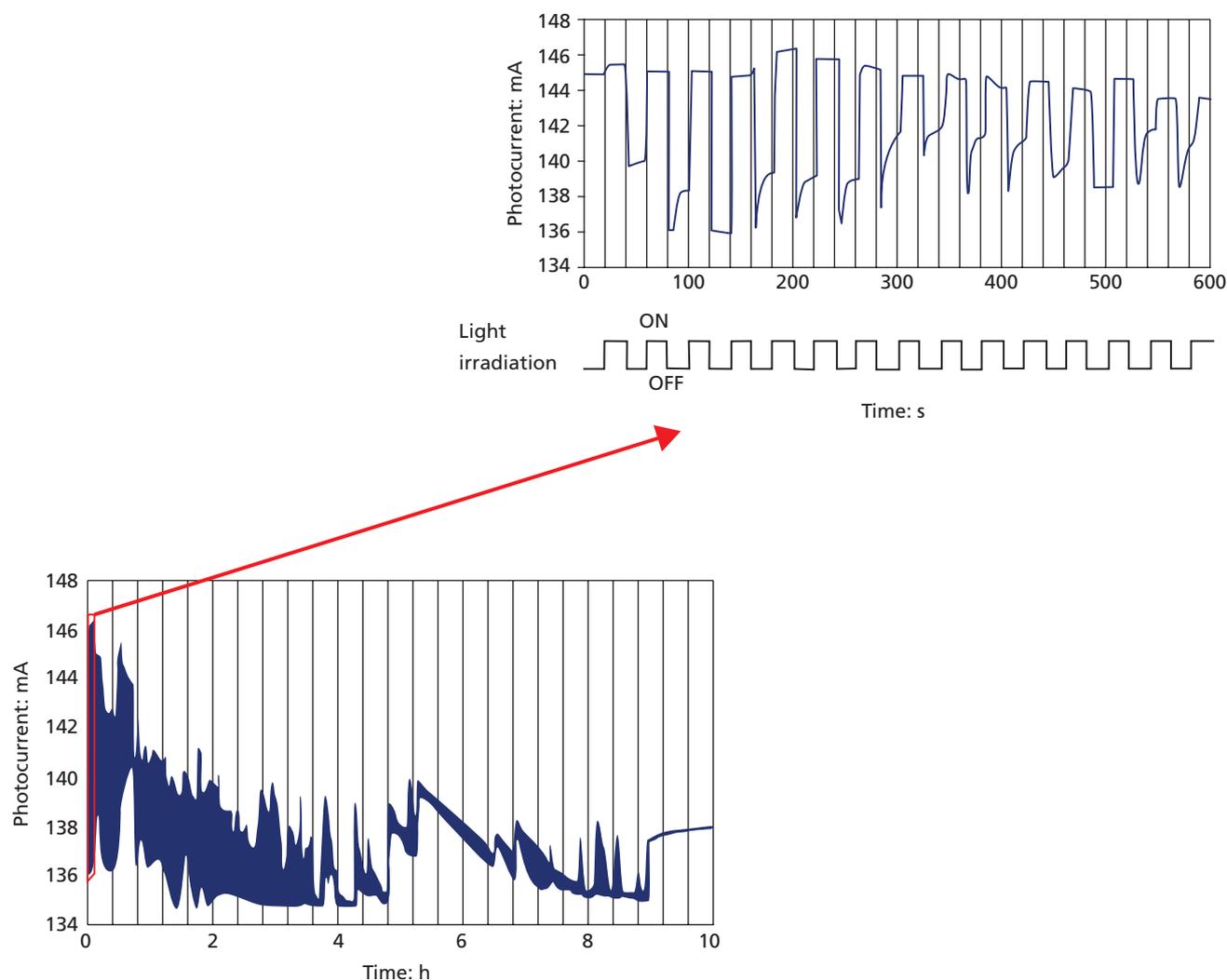


Figure 7. Photocurrent of indium tin oxide/gold photoreceptive device using self-assembled film.

4. Results

The authors stabilized the RA solution because its state changes over time and studied the optimization of the chitosan solution. The RA dissolved in an aqueous ethanol solution. The RA molecule maintained a stable monomolecular state in a concentration of more than 50 v% ethanol (EtOH). When the RA solution concentration was less than 50v% EtOH, the RA molecule precipitated in the solution after micelle formation. The authors fabricated a RA–chitosan self-assembled film using a RA mixed solution and by changing the pH (3 and 5) and EtOH concentration (10, 30 and 50 v%). In 10 and 30 v% EtOH, RA formed micelle ($\lambda_{\max} = 400$ nm), and in 50 v%, it existed as a monomer ($\lambda_{\max} = 350$ nm) in the mixed solution (40 $\mu\text{mol/l}$). In pH 6 through pH 9, RA existed as a monomer ($\lambda_{\max} = 340$ nm), and in pH 4, it formed micelle ($\lambda_{\max} = 395$ nm) in a water solution (40 $\mu\text{mol/l}$). These association states in each conditioned solution are schematically shown in Figure 6, and corresponding spectra are also shown.

The reproducibility of photo-receptive devices was improved from 10 to 33% using a RA–mixed solution (in pH 3, 400 $\mu\text{mol/l}$, 50 v% EtOH). Under the same conditions, the photocurrent value of the devices increased from 4.0 to 7.0 mA. One of the best responses of these manually fabricated photoreceptive devices was that the photocurrent was averagely and typically 7 mA in the beginning area in good response, and the photocurrent response continued during the longest period to date, which was 9 h, as shown in Figure 7. This is an 81 times longer life-time than previously reported.

4.1 Estimation of external quantum efficiency of photocurrent response

The authors calculated the external quantum efficiency of the photocurrent response for the devices that performed the best by using Equation 1.

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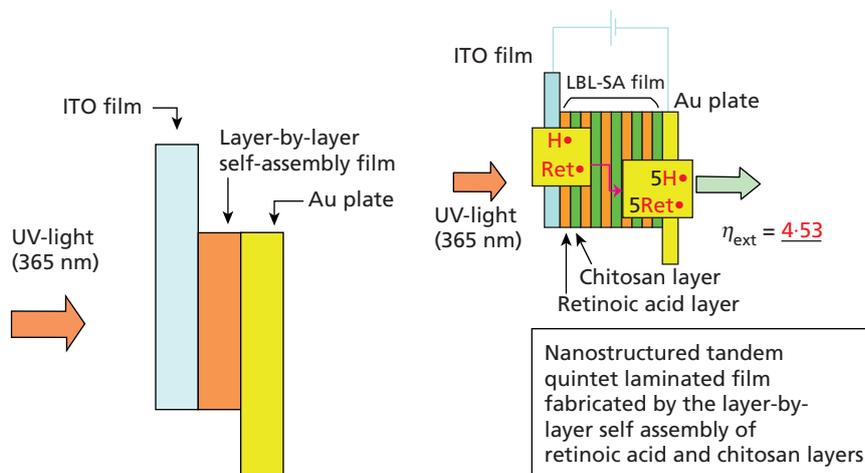


Figure 8. Mechanism of high external quantum efficiency of photocurrent response of biophotonic devices

Bias: V	After preparation: d	Photo current: mA
4	0	1–2
1	0	1–2

Data adapted from Ref.⁵

Table 2. Photocurrent response dependency on applied voltage

$$1. \quad h_{\text{ext}} = (hcI_{\text{pd}}) / (e\lambda P_{\text{in}})$$

where η_{ext} is the external quantum efficiency, h is the Planck's constant (6.626×10^{-34} J-s), c is the light speed (3.0×10^8 m/s), I_{pd} is the photocurrent, e is the electron charge (1.602×10^{-19} C), λ is the wavelength of the irradiated light (3.65×10^{-7} m) and P_{in} is the light-receiving power. In the best response case obtained experimentally, photocurrent I_{pd} was averaged and typically 7 mA, the density of the light-receiving power was $700 \mu\text{W}/\text{cm}^2$, the surface area of the LBL film was 7.5 cm^2 , and therefore, the power of light-receiving P_{in} was calculated out as 525 mw. From the experimentally obtained date, the external quantum efficiency of the photocurrent response h_{ext} for the best device was 4.53. In comparison, the efficiency h_{ext} was 0.65 when using an automatic layer-by-layer self-assembly machine ($I_{\text{pd}} = 1$ mA). In addition, the efficiency h_{ext} for one of the gel-type devices was 0.004 ($I_{\text{pd}} = 6.3 \mu\text{A}$).

4.2 Consideration

The authors determined that the external quantum efficiency of 4.53 was obtained by using the radical reaction process in a nanostructured laminated film fabricated by using the layer-by-layer self-assembly process. The light illumination generated

hydrogen and RA radicals in the first layer. These radicals generated five radicals each in each of the five layers as a chain reaction, and five RA radicals terminated by accepting electrons from a negative electrode and changed into RA anions. Five hydrogen radicals also terminated by donating electrons to a positive electrode and changed into H^+ ions. The RA anions and H^+ ions recombined and responded repeatedly to the light illumination as schematically shown in Figure 8. On the other hand, in gel-type devices, there is no tandem multiple laminated film with nanostructures formed by using layer-by-layer self-assembly of RA and chitosan. Therefore, the external quantum efficiency is very low at 0.004.

The authors have reported the dependency of photocurrent response on applied voltage.⁴ When 4 V was applied to a sample prepared just after fabrication, it was about 1–2 mA and when 1 V applied it was also about 1–2 mA. These are summarized in Table 2 on referring to Ref.⁵. It is clear that there is no dependency of photocurrent response on applied voltage in the LBL-SA biophotonic device. These phenomena support the mechanism for the photocurrent response of biophotonic devices created by radical reaction rather than ionic or charged carrier reaction.

5. Conclusion

The authors fabricated photoreceptive devices using RA and chitosan under optimized conditions by using a layer-by-layer self-assembly process. The reproducibility of photo-receptive devices was improved from 10 to 33% using an optimized RA mixed solution. The photocurrent value of devices increased from 4.0 to 7.0 mA. One of the best responses of these manually fabricated photoreceptive devices was that the photocurrent was 7 mA and the photocurrent response continued during the longest period to date, which was 9 h. This is an 81 times longer life-time than any previously reported. The authors calculated the

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external quantum efficiency of the photocurrent response for the devices that performed the best. The estimated external quantum efficiency of the photocurrent response for the best device was 4.53. In comparison, for one of the gel-type devices, the efficiency was 0.004. The mechanism for the photocurrent response of biophotonic devices seems to be the radical reaction rather than an ionic or charged carrier reaction. Tandem multiple laminated nanostructures created using the layer-by-layer self-assembly of RA and chitosan are useful for ensuring the high quantum efficiency of the photocurrent response of biophotonic devices.

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REFERENCES

1. Ben-Nun, M.; Monlar, F.; Lu, H.; Philips, J. C.; Martnez, T. J.; Shulten, K. Quantum dynamics of retinal's femtosecond photoisomerization in bacteriorhodopsin. *Faraday Discussions* **1998**, *110*, 447.
2. Hargrave, P. A. Rhodopsin structure, function, and technology. *Investigative Ophthalmology & Visual Science* **2001**, *42*, 3.
3. Kandori, H.; Shichida, Y.; Yoshizawa, T. Photoisomerization in rhodopsin. *Biochemistry (Moscow)* **2001**, *66*, 1197.
4. Tsuchida, Y.; Ikeda, Y.; Kobayashi, N.; Arakawa, T.; Yamano, S.; Mitachi, S. Photo-sensitivities of immobilized retinoids. *Japanese Journal of Applied Physics* **2009**, *48*, 032402.
5. Tsuchida, Y.; Hidaka, A.; Mitachi, S. Photocurrent response of photoreceptive devices using a retinoid immobilized in a chitosan gel film. *Japanese Journal of Applied Physics* **2010**, *49*, 127003.

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