Micro and Nano Systems Letters

LETTER

Open Access

Non-fullerene acceptor based photoelectric material for retinal prosthesis

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Abstract

Microelectronic retinal implants can restore a useful level of artificial vision in photoreceptor-damaged retina. Previously commercialized retinal prostheses require transocular connection lines to an external power supply and/or for data transmission, which are unwieldy and may cause unwanted side effects, such as infections. A recently reported wireless device used a rigid silicon substrate. However, it had the potential for a long-term mechanical mismatch with soft retinal tissue. In this work, we used organic photovoltaic materials which can be fabricated on flexible substrates as well as be operated without any physical connection to the external world. The present study employed PCE10 as an active layer for retinal prosthetic application for the first time. Compared to previously studied organic photovoltaic materials used in retinal prosthesis research (such as P3HT), our PCE10 devices showed higher efficiency, providing a huge advantage in this field. When the PCE10 was blended with other non-fullerene acceptors achieving a ternary organic photovoltaic layer (PCE10:ITIC:Y6 blend), it showed lower reduction of photocurrent under same irradiation frequency condition. The fabrication method for our organic photovoltaic device was simple and easy to control its thickness. The fabricated devices showed adequate photocurrent to stimulate the retinal neurons with a smaller reduction in generated photocurrent during repeating stimuli compared to P3HT or PCE10 alone.

Keywords Photovoltaic, Non-fullerene acceptor, Retinal prosthesis, Ternary organic photovoltaic materials

Introduction

Retinal prostheses have emerged as a promising approach to restore vision in patients with outer retinal degenerative diseases [1–3]. However, due to their sub-optimal performance, significant effort has been dedicated to developing a better understanding of electrically-evoked spiking responses of retinal ganglion cells (RGCs) [4] and to optimizing electrical stimulation conditions [5–8]. There are still numerous challenges that remain to be addressed [9], which include a comprehensive understanding of how degenerate retinas respond to electric stimulation [10], how those electrically-elicited spiking activities transmit new artificial visual information [11], and so on. Most of all, retinal prostheses require further development of miniaturized high-density electrode arrays to provide high-resolution artificial vision for patients. Regarding the development of new hardware, structural limitations need to be addressed. For example, previously commercialized retinal prostheses have incorporated interconnecting wires which pass through the eyeball to connect with external power and/or for data transmission [1–3], which may cause unintended side

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effects such as inflammation and infections in addition to being cumbersome and uncomfortable for patients. Although wireless devices built on rigid Si substrates have recently emerged to address this issue, however, there is a potential long-term mechanical mismatch between them and the soft and flexible retinal tissue, which can lead to device failure and further complications. Therefore, there is a need for the development of flexible and biocompatible devices that can operate wirelessly and reliably within the retinal environment.

An additional challenge is that large electronic components required for implantation increase surgical complexity and the potential for side effects [12]. Electromagnetic coils are typically used to supply power and regulate voltage and current, however, their size and mass limits the ability of users to make natural eye movements for interpreting artificial visual information [13]. The use of photovoltaic materials may address these issues by converting light directly into current within implanted devices. In particular, organic semiconductors are more flexible and lighter than inorganic semiconductors, making them attractive for implant applications. Also, they can easily be fabricated with thin film deposition and have low production costs. In past studies, P3HT and PCBM have been used for retinal prosthetic applications [14]; however, other organic semiconducting materials exist which show better photovoltaic performance [15]. For instance, PCE10 is a representative donor material used in two-component organic photovoltaic (OPV) devices that utilize donor and acceptor materials in the active layer [16]. Upon light absorption, excitons are formed and separated into free charges at the donor-acceptor interface. The resulting free charges are driven to opposite electrodes due to the internal potential difference created by the work function difference between the electrodes [17]. By adding a third organic material, the absorption spectrum of the device can be tuned, and the energy level alignment between the donor and acceptor can be adjusted to improve device performance [15, 18].

In this study, we have investigated the use of a ternary organic photovoltaic layer (PCE10:ITIC:Y6 blend) for self-powered retinal prostheses. The three-component OPV was shown to generate current in response to light, demonstrating the potential for the device to function as a power source for retinal prostheses. The use of a photovoltaic response eliminates the need for external power supplies and simplifies device architecture, thus improving the feasibility of implantation. These findings suggest that three-component OPV materials have the potential for the development of next-generation retinal prostheses.

Methods

Materials

PCE10 (CAS No. 1469791-66-9; i.e., Poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b;4,5-b′]dithiophene-2,6-diyl-alt-(4-(2-ethylhexyl)-3-fluorothieno[3,4-b]thiophene-)-2-carboxylate-2-6-diyl)], ITIC (CAS No. 1664293-06-4; i.e., 3,9-bis(2-methylene-(3-(1,1-dicyanomethylene)-indanone))-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-d:2′,3′-d′]-s-indaceno[1,2-b:5,6-b′]dithiophene), and Y6 (CAS No. 2304444-49-1; BTP-4F) (i.e., 2,2′-((2Z,2′Z)-((12,13-bis(2-ethylhexyl)-3,9-diundecyl-12,13-dihydro-[1,2,5]thiadiazolo[3,4-]thieno[2″,3″:4′,5′]thieno[2′,3′:4,5]pyrrolo[3,2-g]thieno[2′,3′:4,5]thieno[3,2-b]indole-2,10-diyl)bis(methanylylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1*H*-indene-2,1-diylidene) dimalononitrile) were purchased from Ossila (Sheffield, United Kingdom). Poly(3-hexylthiophene-2,5-diyl)) (P3HT) for comparison was purchased from Sigma-Aldrich (St. Louis, MO, USA). All solvents were purchased from Samchun Chemical (Seoul, South Korea) and used as received.

Photovoltaic device fabrication

We fabricated photovoltaic devices consisting of Au (100 nm), an organic active layer (110 nm), and indium tin oxide (ITO). We prepared samples with three different organic layers: PCE10 only (Fig. 1a), P3HT only (Fig. 1b), and PCE10:ITIC:Y6 blend (Fig. 1c) for comparison. After cleaning an ITO glass substrate with distilled water, acetone, isopropanol, and ethanol under ultrasonication successively for 40 min, the top surface of the substrate was treated with ultraviolet (UV)/Ozone light for 20 min. All organic layers were spin-coated onto the ITO glass substrate in a glovebox. We prepared organic semiconductor solutions in a glovebox under a nitrogen atmosphere, which were stirred overnight at 70 °C (dissolved in anhydrous chlorobenzene with a concentration of 30 mg/mL). These solutions were spin-coated at 3000 rpm for 60 s and heat-treated on a hot plate at 130 °C for 20 min. A layer of Au (100 nm) was deposited via an e-beam evaporator with a shadow mask. The device was then encapsulated with polydimethylsiloxane (PDMS), excluding the center part of the deposited gold electrode (Fig. 1).

Device characterization using a patch-clamp recording system

We used a patch-clamping recording system to measure photocurrent near the top gold surface. First, glass pipettes were prepared using a micropipette puller (Model P-97, Sutter Instrument, Novato, CA, USA) and utilized as patch electrodes with resistances ranging from 8 to 12 MΩ. Two chloride-coated silver wires shaped as balls were positioned at the two opposite

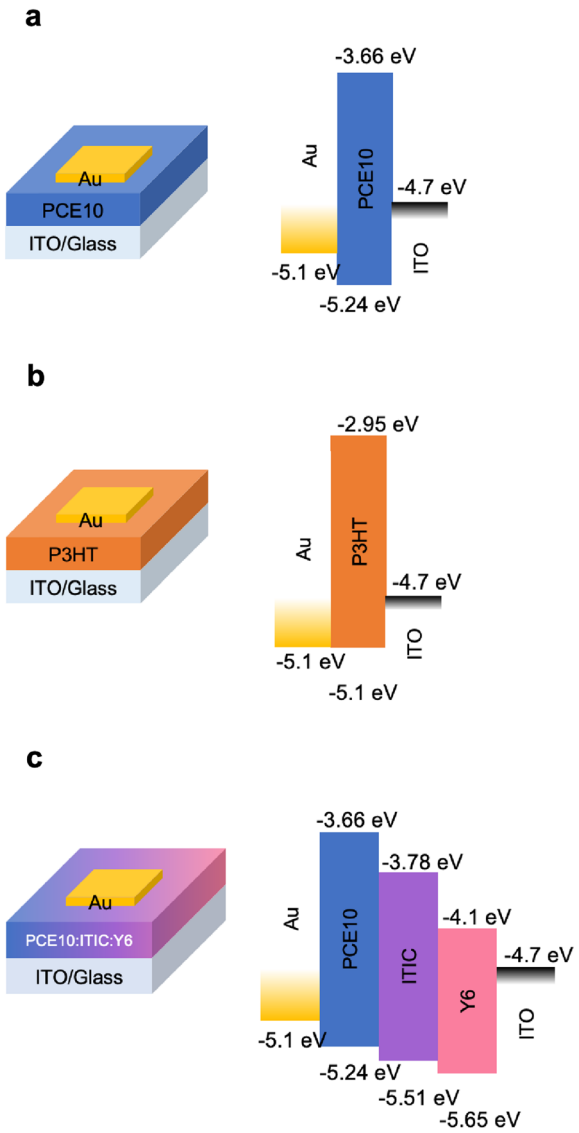

Fig. 1 Structure and energy band diagram of each photovoltaic device for retinal stimulation. Electrodes are the same with ITO and gold pair. Active layer varies; **a** PCE10, **b** P3HT, and **c** PCE10:ITIC:Y6 blend

edges of the recording chamber to serve as ground electrodes. A micromanipulator (MPC-200, Sutter Instrument, Novato, CA, USA) was used to carefully position the electrode tip approximately 25 µm above the Au surface (Fig. 2). The acquired data were low-pass filtered at 2 kHz using an amplifier (MultiClamp 700B, Molecular Devices, Sunnyvale, CA, USA) and digitized by a data acquisition card (PCI-MIO-16E-4, National Instruments, Austin, TX, USA). The measurements were conducted in Ames' medium (Sigma-Aldrich, St. Louis, MO, USA) which is commonly used for retina electrophysiology recordings. The data acquisition and electrical stimuli were controlled by custom software written in LabVIEW (National Instruments, Austin, TX, USA) and MATLAB (MathWorks, Natick, MA, USA).

Light stimulation for fabricated device

We irradiated the device placed inside a chamber filled with Ames' medium using a 450 nm LED (M450LP1, Thorlabs), with a light intensity of 36.19 µW/mm^2. The intensity of light, the exposure time and frequency were systematically varied.

Results and discussion

We conducted measurements of electrical artifacts resulting from photovoltaic currents in response to 5-second-long light stimuli. The photocurrents were indirectly calculated by comparison with electric artifacts measured in response to known current amplitudes delivered by a stimulus generator (STG2004, Multi-Channel Systems GmbH, Reutlingen, Germany). To apply a known current, we used platinum-iridium electrodes (MicroProbes, Gaithersburg, MD, USA) with a resistance of 10 kΩ, which had a conical tip with dimensions of approximately 125 µm in height and 30 µm in base diameter and lacked insulation at their upper section. The surface area of each electrode was approximately 5900 µm^2. We compared the photovoltaic performance of two organic active layers, PCE10 and P3HT, which are novel and conventional organic active materials for retinal prosthetic applications, respectively.

Both devices exhibited an monontonic trend in photocurrent as the intensity of light increased (Fig. 3a). Specifically, as the light intensity increased from 20 to 100% (36.19 µW/mm^2), the peak photocurrent amplitude of PCE10 increased linearly from 10.6 to 194.5 pA/cm^2, while P3HT showed an increase from 6.0 to 69.5 pA/cm^2. Given the fact that P3HT has successfully evoked spiking activities in retinal ganglion cells *ex-vivo* in response to external light stimulation [14], our results suggest that the PCE10 can generate sufficient photocurrent as a novel organic material for retinal prosthesis. Although the photocurrent seemed to be sufficient, due to the limitation of our optical setup, we illuminated light from the top through the thin gold layer which attenuated ~ 70% of light intensity. Therefore, future researches would be needed to adapt an ultrathin gold layer [19, 20] or to change our optical setup to deliver light stimuli from the bottom through the ITO layer.

To characterize the relationship between the stimulation duration and photocurrent, we illuminated devices for variable amounts of time by changing irradiation frequencies (Fig. 3b). As the irradiation time decreased, the photocurrent peak amplitude of P3HT decreased

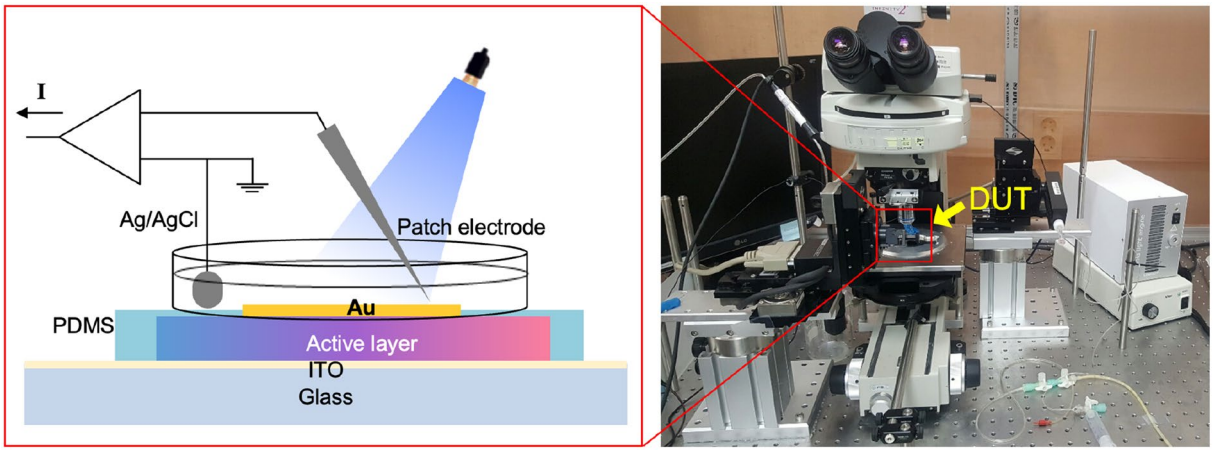

Fig. 2 Photocurrent measurement setup using patch-clam recording technique. Photocurrent from the device was measured by a patch electrode. Light of 450 nm in wavelength was illuminated from top. A measurement setup photo is shown in the right

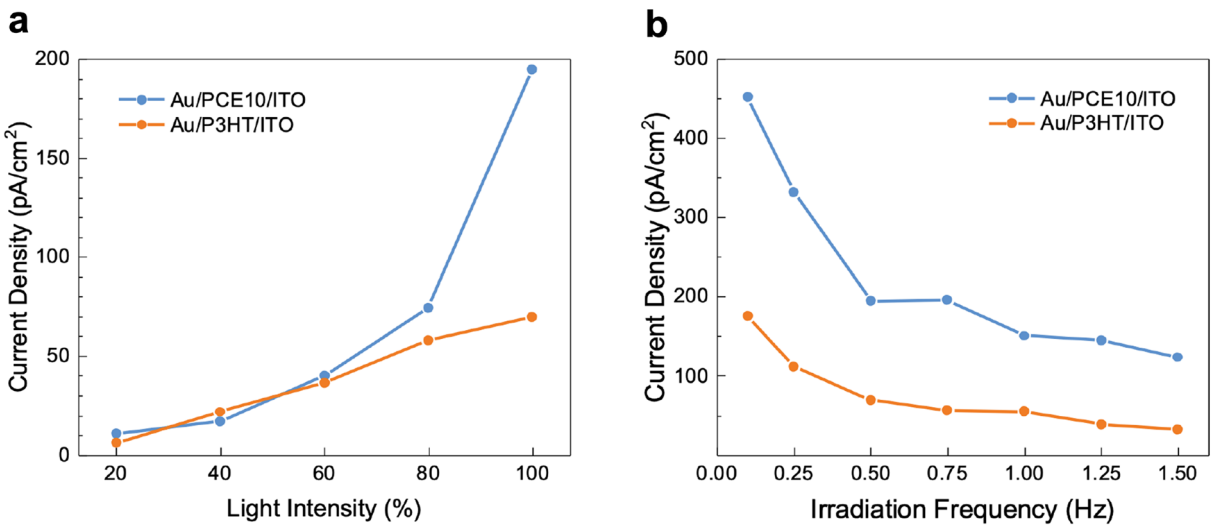

Fig. 3 **a** Photocurrent of the device as a function of light intensity. PCE10 showed higher efficiency than P3HT especially under the strong optical power. **b** Photocurrent as a function of light irradiation frequency. The performance of PCE10 was higher than that of P3HT over the whole range of irradiation frequency we tested

exponentially from 175.3 to 32.4 pA/cm^2, while that of PCE10 changed from 451.8 to 123.7 pA/cm^2. The performance of PCE10 was higher than that of P3HT over all irradiation frequencies (or time periods). In particular, when the irradiation time was the longest (the left-most data points in Fig. 3b), the photocurrent of PCE10 was significantly higher than that of P3HT. We confirmed that the photocurrent was modulated by the duration of light exposure.

Given the better efficiency of PCE10, we introduced non-fullerene acceptors (ITIC:Y6) to further enhance the device's performance. With these acceptors, electrons can be efficiently diffused when an exciton is generated. We tested the reproducibility of photocurrent responses upon repetitive illumination for all devices (Fig. 4). The reduction rate was defined as a percentage by subtracting the photocurrent arising from the last illumination from the photocurrent arising from the first illumination. At 0.5 Hz, the ternary material showed a decay rate in the late twenties (middle gray bar of Fig. 4), similar to that of PCE10 only (left gray bar of Fig. 4) and better than that of P3HT alone (right gray bar of Fig. 4). When devices were illuminated with 5-second-long light pulses delivered at 0.1 Hz (20 repetitions), the photocurrent of the

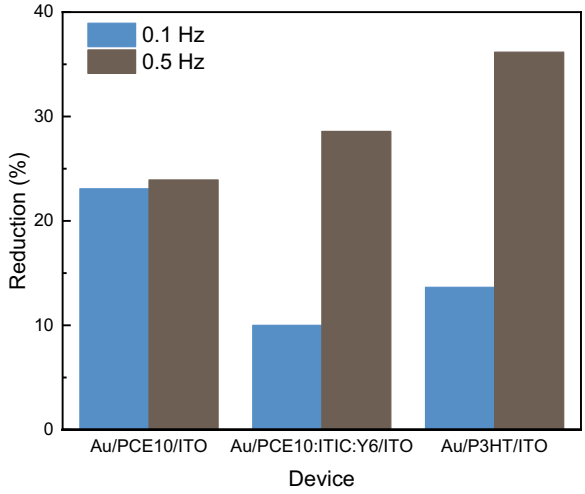

Fig. 4 Photocurrent reduction after 20 times repetition in each frequency. The average reduction of PCE10 device was lower than that of the P3HT device. The ternary blend device demonstrated the lowest reduction under lower irradiation frequency

ternary material device demonstrated the least reduction around 10% decrease (middle blue bar of Fig. 4). This small reduction in the photocurrent generated by the subsequent illuminations suggests that the ternary material would be suitable for repeating stimuli with minimal fading of artificially-evoked visual percepts. For a high open-circuit voltage and power conversion efficiency, it is important to identify donor materials with moderate band gaps and deep highest occupied molecular orbital (HOMO) levels [21]. The HOMO level of PCE10 is lower than that of P3HT; we also used suitable acceptor materials that have lower HOMO levels. These seem to result in well-matched work functions, enhancing reliable charge diffusion within our optoelectronic devices.

Conclusion

In this study, we have successfully developed a ternary photovoltaic material for retinal prosthetic application and have conducted the first measurements of its generated photocurrent. Our results demonstrate that the amount of photocurrent generated can be precisely controlled by adjusting the intensity and frequency of light. Additionally, the ternary device showed increased stability during repeated light exposure. The ability to control current through light intensity provides the potential to more precisely deliver electrical signals, allowing for the implementation of arbitrary image contrasts.

To further improve the precision of the device, future research could focus on improving the shape and material of the electrode that delivers electricity to the cells for retinal neuron stimulation. The use of a variety of electrode shapes and PCE10-based ternary photovoltaic materials could lead to the development of a light-switching artificial retina device that can be implanted in the eye. In such a device, visual information could be finely adjusted simply using light, rather than applying voltage to each electrode as in traditional artificial retina devices. This potential breakthrough could significantly improve the quality of life for those with retinal degeneration.

In conclusion, our study presents a new approach to developing advanced artificial retina devices. The utilization of organic photovoltaic materials and light-controlled current will open up new possibilities for the restoration of visual function in patients with retinal degeneration. Further research will explore the use of multiple layers of organic photovoltaic materials to further enhance device performance and biocompatibility, and ultimately provide a more effective and reliable solution to restoring vision in patients with retinal degeneration.

Abbreviations

P3HT	Poly(3-hexylthiophene-2,5-diyl))
UV	Ultraviolet
ITO	Indium tin oxide
PDMS	Polydimethylsiloxane

Acknowledgements

The authors would like to thank Na Min An for her technical discussions.

Author contributions

HS and JYK fabricated the devices. HR and HS conducted the cell-attached patch clamping experiments and analyzed the data. HS and HR drafted the figures and manuscript. BCL, BW and MI supervised the all experiments and data analyses. MI designed the study and revised the figures and manuscript. All authors reviewed and approved the final manuscript before submission.

Funding

This work was supported by the National Research Foundation of Korea (NRF) Grants 2020R1C1C1006065, 2021M3F3A2A01037366, and 2022M3E5E8017395 funded by the Korean Government (MSIT).

Availability of data and materials

The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interests

The authors declare that they have no competing interests.

Received: 16 August 2023 Accepted: 22 September 2023
Published online: 28 September 2023

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