BIOMIMETIC PHOTODIODE DEVICE WITH LARGE PHOTOCURRENT RESPONSE USING PHOTOSYNTHETIC PIGMENT-PROTEIN COMPLEXES

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ABSTRACT

Efficient light to energy conversion was demonstrated in solid-state, lateral photodiodes device containing photosynthetic light harvesting chlorophyll protein complexes as active materials. The device exhibits the highest reported photocurrent density response of 365 μA/cm^2 when illuminated at 320 mW/cm^2 radiation source power. The photocurrent response was stabled over 10^4 s of continuous cycles of dark and illumination states. The short rise and decay time of the photocurrent waveform within sub-second range indicates an effective photogeneration and charge extraction within the device. Optical bandgap extraction using absorbtion coefficient method reveals that the energy gap of the active materials ranges from 2.8 to 3.8 eV, correspond to the Photosystem I and Photosystem II of the photosynthetic pigmen-protein complexes.

Keywords: Photocurrent; Photodiode; Photosynthesis; Chlorophyll; PSI; PSII

Introduction

Efficient light-to-energy conversion in photosynthesis has inspired the quest for an efficient, clean and renewable energy source of the future. In the heart of photosynthetic process, the reaction centers (RCs) facilitates photo-induced charge separation with a quantum yield near unity.[1] The highly efficient process relies on the seamless organization of light-harvesting pigments, protein complexes and molecular functional groups held in precise geometries, wherein the molecular electronic states are intricately arranged to enable the unidirectional flow of charges.

Early work on bioinspired optoelectronics system employed photosynthetic pigment as active materials in metal-chlorophyll-metal devices.[2-4] However, the device showed rather unsatisfactory performance with efficiency below 0.5%. The absence of charge acceptor moieties within the active layer was caused this low performance. The subsequent improvement on device performance was realized when n-type or p-type semiconductor material[5-6] was introduced along with chlorophyll. A modest power conversion efficiency of 2.3% is achieved when chlorophyll mixed with C70.[6] In all of these studies the researcher failed to perceive photosynthesis as a whole interconnected system, which resulted in a modest efficiency of the system. In the natural setting of photosynthesis, light is absorbed by the antenna complex of Photosystem II (PSII) to be funneled to the photosynthesis reaction center P680. PSII antenna consists of protein-embedded chlorophyll to absorb light and carotenoids to quench excess radiation energy. The funneled energy excites the electron of P680 into an excited P680* state. The process is quickly followed by electron transfer from P680* (formed P680+) to the primary electron acceptor pheophytin, quinone

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molecules Q_A-Q_B, and plastoquinone to cytochrome b6f protein complex. Subsequently the charge is transferred by phthalocyanine to P700 reaction center of Photosystem I (PSI) and then ferredoxin for ATP generation. The redox process is completed when P680+ regains electron from splitting of water molecules into oxygen and protons.[1]

Most recently, the biomimetic strategy has been borrowed from photosynthetic organisms utilizing the whole photosynthetic pigments and proteins to be incorporated into the man-made photocurrent devices.[7-13] Thereby, the high efficiency of the photosynthesis might be retained in the artificial devices. Bilayer structure of recombinant ferredoxin and chlorophyll shows one directional transport of electron from chlorophyll to ferredoxin molecule during visible light exposure.[7] Similarly, at the time photosynthetic carotenoids introduced to the bulk hetero-junction solar cell, it helps to quench the excessive radiation detrimental to photocurrent generation.[8] Recently, by employing bacterial photosynthesis reaction center (RC)-light harvesting core complex (LH 1) immobilized onto the Gold electrode, a relatively high photocurrent density of 7.1 $\mu A/cm^2$ had been achieved in a bio-photo-electro-chemical cell structure.[9] An improvement in photocurrent density up to 10 $\mu A/cm^2$ was obtained when the protein was suspended into the supported lipid bilayer.[10] The highest photocurrent density response of 45 $\mu A/cm^2$ is obtained when the protein complex was densely packed via Langmuir film deposition.[11] Most of these works were conducted in bio-photo-electro-chemical cells which required electrolyte solution and must be confined and sealed. Up to now, only one work reported the solid-state bio-photovoltaic device albeit the inferior device performance.[12]

Herein, we demonstrated a solid state biomimetic photodiode device with large photocurrent responses. The active material was attained from the Alfalfa leaves extract which retained the photosynthetic pigments and proteins complexes. Large photocurrent density response of 188 $\mu A/cm^2$ was achieved under 320 $\mu W/cm^2$ fluorescent radiation power. The devices showed stable photocurrent responses without significant reduction in performance under continuous cycling test for 10^4 seconds.

Methods

Extract of Alfalfa (*Medicago sativa l.*) leaves was obtained from K-Link K-Liquid Chlorophyll containing 4% leaves extract in aqueous solution. The leaves extract retained its photosynthetic pigments and proteins complexes including the PSI, PSII and cytochrome b6f. The used leaves extract was without further purification. A lateral metal-organic-metal photodiode device was obtained by spin coating or drops-casting of the leaves extract solution onto patterned Cu electrode. The equivalent electrode length was 32 mm while the electrode gap was 0.05 mm. The leaves extract was drop-casted onto the gap and allowed to dry at room temperature and ambient condition. The drop-casted film of leaves extracts was also prepared on a glass substrate with exact amount for spectrophotometric studies. Prior to leaves extract deposition, the substrates were rinsed with ethanol and deionized water and dried at room temperature.

The optical properties, including transmittance, absorbance, and optical band-gap of the pigment-protein complexes were recorded by using Hitachi U-2900 Spectrophotometer on UV and visible wavelengths from 190-950 nm. Optical band-gap extraction was performed on the aqueous solution pigment-protein complexes sample at various concentration whereas other data were obtained from the thin-film samples. Photocurrent response measurements were performed by manually exposing and covering the device to a 40 Watt fluorescent lamp. Voltage and current response were recorded by using PC Link Digital Multimeter VA18B. To evaluate the photocurrent response, the resistance across the device was measured against time during the dark and illumination states at various

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light intensities. Cycling endurance test of the photodiode was performed by monitoring the photocurrent response as the device subjected to continuous cycles of dark and illumination.

Result and Discussion

Figure 1 shows the absorbance spectra of the leaves extract in the solution and film forms. The large absorbance peak around 214 nm corresponds to the absorbance by the antenna complexes of PSI and PSII.[13-14] It shows that most of the PSI and PSII protein complexes are still intact within the leaves extract. The absorbance peak around 400 nm and the red maxima at 661 nm signify the presence of molecular chlorophyll.[15] The leaves extract also contains several carotenoids mainly β-carotene, lutein, neoxanthin and violaxantin.[15] The large discrepancies between the blue absorption and red absorption of chlorophyll suggest that the carotenoid presents at much higher amount compared to unbound chlorophyll molecules. The Large absorption peak of PSI and PSII also suggest that most of the chlorophyll molecules are bounded to the protein complexes.

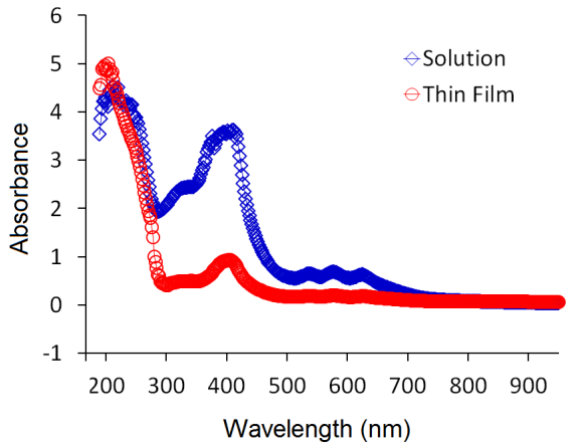

Figure 1. The absorbance spectrum of Alfalfa leaves extract containing the light harvesting chlorophyll-protein complexes in the aqueous solution and thin film forms

Note that the similarity of the absorbance spectra of the solution and the film form indicates that the leaves extract deposition process do not alter much on the structure and composition of the photosynthetic protein complexes PSI and PSII. The 214 nm peak retains its high absorbance whereas the reduction of 400 nm peak shows that the carotenoids contents decrease in the film forms. As the thickness of the film increases, the absorbance increases accordingly and thus generates higher photocurrent response when illuminated. However, increasing the film thickness also causes an increase in the dark current level, which is unfavorable. Taking into consideration the trade-off between photocurrent and dark current level, an optimized film thickness of 1.5 μm is employed for subsequent studies.

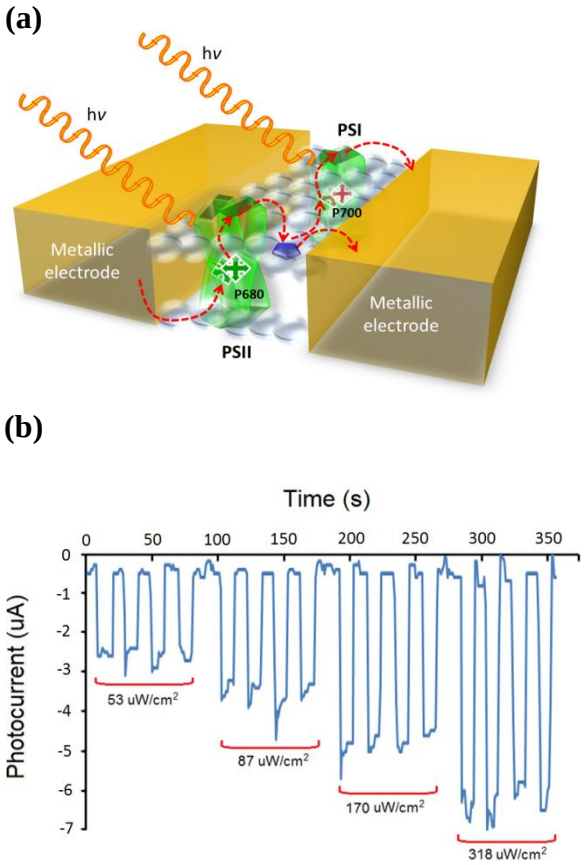

Figure 2. (a) Schematic structure of the lateral photodiode devices. The active material of light harvesting chlorophyll-protein complexes are deposited into the narrow electrodes gap (b) The photocurrent response of the device measured under polychromatic fluorescence lamp at various intensities

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Figure 2(a) depicts the biomimetic photocurrent process employed in this work. Light radiation is absorbed by the antenna complex of PSI and PSII. The absorbed energy is used to excite electrons from reaction centers P680 and P700. Further, the electrons follow the charge transfer path through several proteins and transport molecules to be collected in the anode. To complete the redox process, electrons are injected from the cathode to reduce the P680+ and P700+ to its original state. Figure 2(b) shows the photocurrent response of the device during dark and illuminated state. The device was initially in dark state and then exposed fluorescence illumination for 10 s. Subsequently, the device was put in dark state for 10 s to allow for relaxation. The dark-illumination cycles were repeated several times to obtain a representative reading. The photocurrent response is observed to increase linearly with light intensities. A 50 mW/cm^2 light intensity generates photocurrent density response of 162 µA/cm^2. Increasing the light intensities to 90 and 170 mW/cm^2 resulted in an increase of photocurrent density level to 206 and 300 µA/cm^2 respectively. Large photocurrent density response of 365 µA/cm^2 is achieved when 320 mW/cm^2 light intensity is used.

The photocurrent response exhibits a sharp, square-shaped waveform with very short rise time and decay time in the sub-second range as shown in Figure 3(a). It indicates an efficient charge transfer between the protein complexes and the electrodes where most of the photo-generated electrons are extracted from the electrode.[16] These results show superior performance compared to the previously reported work on similar systems where the waveform showed a non-saturating profile with long rise and decay times in the order of minutes.[9-11] To evaluate the endurance of the photocurrent response, cycling stability test was performed by monitoring the photocurrent response as the device continuously cycled between dark and illuminated states. For cycling test, the light intensity was fixed at 320 mW/cm^2. The cycling endurance test result is shown in Figure 3(b). Both the dark current and photocurrent responses show relatively stable reading over the cycling test period of 10^4 s. This finding revealed that the pigment-protein complexes obtained from the Alfalfa leave extract are photo-active.

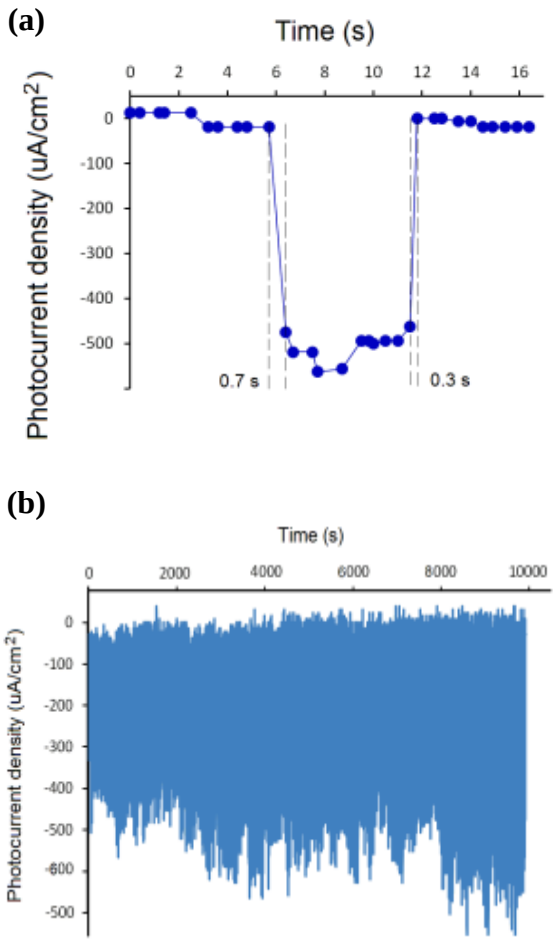

Figure 3. (a) Enlarged view of the photocurrent switching signal reveals rapid rise time and decay time dynamics of the active material (b) Photocurrent response of the device under continuous cycling test for 10^4 s. The light intensities were fixed at 320 mW/cm^2.

Optical band-gap of the active material is extracted from the intercept of the graph to the photon energy axis in $(\alpha h\nu)^2$ against the photon energy ($h\nu$) plot as shown in **Figure 4**. For the film sample, there are two major energy-gap observed within the 2.8 eV and 3.8 eV bands. These observed band-gap

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values correspond to the blue absorption of PSI, PSII, and Light Harvesting Antenna Complexes (Lhc) of photosynthetic protein complexes as reported in the literature.[17-18] The result shows that the active material retains its photo-activity even in the solid-state thin film forms.

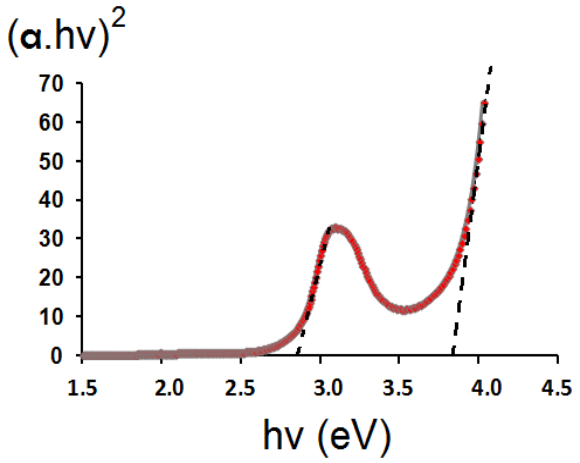

Figure 4. Optical absorption curves of pigment-protein complexes from Alfalfa leaves extract at various film thickness.

There were at least three factors that make this work distinct from the previously reported works. In this work, complete set of photosynthesis chlorophyll-protein complexes including its transport molecules was employed instead of individual component. In addition, our device is in a solid-state form in which the absence of liquid electrolyte eliminates the unnecessary capacitive double layer effect commonly encountered in the electrochemical device structure.[19] Lastly, the lateral structure of the device prevents degradation of the active organic layer as it eliminates the needs to deposit the top electrode above the active materials.

Conclusion

To conclude, a large photocurrent response from light-harvesting chlorophyll-protein complexes thin film devices has been demonstrated. The device exhibits large photocurrent density response of 365 uA/cm^2 which has the highest among reported results based on solid state devices. The sharp, square-shaped photocurrent waveform with short rise and decay time indicates that the photogeneration and charge extraction occur in an effective manner. The photocurrent response shows excellent cycling stability when cycled continuously under dark and illumination states up to 10^4 s. These findings envision greater accommodation of bio-inspired bio-photo-electro-chemical concepts towards high-performance solar energy harnessing, solar fuel generation, and other optoelectronic devices applications.

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