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Organic solar cell based on photosystem I pigment-protein complex, fabrication and optimization

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ABSTRACT

The trends of using biological materials in electronic devices have made great developments in the last few years. Furthermore, the appealed cost features of organic semiconductors represent a bright low-cost, environment compatible, and efficient future for bio & nanotechnologies, especially Bio-organic solar cells which may consider as a noteworthy option for photovoltaic applications. Here, we report a novel single junction organic solar cell based on photosystem I pigment-protein complex. The complex which operated either as photosensitizer and charge generator compound, surprisingly. Photosystem I complexes were extracted from young spinach leaves and used as the active layer of the intended solid-state solar cell device, subsequently. After the characterization of the final cell, our photovoltaic system showed the current density of 3470 μA cm^{-2} which realizes as a notable approach in between photo-system- I based energy conversion systems.

1. Introduction

Organic semiconductors (OSCs) used in optoelectronic applications instead of conventional rare, high cost, and pollutant inorganic compounds have already initiated the substantial interest in the scientific communities [1]. In general, the tunable mechanical and photo-electric properties of organic materials have opened the horizon with an enormous amount of possibilities to produce strong, flexible, and light-weight materials with the potential for mass production. As such, OSCs remain a topic of considerable interest for basic and applied research. Of course, this point of care leads to the generation of organic and hybrid inorganic/organic-based electronics. In respect to previously mentioned trend, LeBlanc and the co-workers [2,3] aligned with their earlier research, report articles which introduced a new bio-based material with interesting optoelectronic properties called photosystem I (PSI) pigment-protein complex.

Inevitably interaction of light in a wide variety of ways with the matter has been considered as a worthwhile and beneficial source of energy production in last decades. One of the most presented light-matter interaction has already known by the name of photosynthesis mechanism. Oxygenic photosynthesis is an operation in which the absorbed light converted into chemical energy through cyclic activities of four multi-subunit membrane protein complexes: PSI, photosystem II (PSII), the cytochrome *b*6f complex, and F-ATPase in cyanobacteria, algae, and higher plants. PSI advantageously involved in both direct and indirect electron transfer reactions. On one hand, the light photons capture through its well-organized peripheral antenna system consisting of pigment networks. Afterward, the excitation energy transfers to the reaction center (RC) where it is used in transmembrane electron transfer reaction. On the other hand, PSII capturing the light and oxidizes the water to produce oxygen and reduce membrane-embedded quinones. The reduced quinones are then utilized by the cytochrome *b*6f complex in the purpose of membrane proton gradient production to reduce donor site of the PSI, copper protein plastocyanin (PC). Afterward, the energy migrates through PSI pigment networks and reaches to P700, a special chlorophyll pair, where electron generation take places [4,24].

Exhibiting a perfect conversion of absorbed photons to electrons (e.g. quantum efficiency) of nearly 100% [25] and notable negative redox potential, arguably introduces PSI as a natural photo-electric compound. This ability of PSI pigment-protein complex to harvest the energy of photons strongly depend on the spatial arrangement of protein subunits and relevant cofactors. Plant PSI made upon 17

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subunits and 193 non-covalently bound photochemical cofactors [5]. 7 nm × 10 nm × 15 nm PSI complex measured by electron microscopy [6] contains extraordinary electron transfer chains (ETCs) begin with P_{700}, the first donor site, and two separated but almost similar branches, A and B. The branches similarly contain A_{cc} chlorophyll molecule (first acceptor/donor site), A_0 chlorophyll molecule (second acceptor/donor site), A_1 phylloquinone, (third acceptor/donor site), and three [4Fe-4S] iron-sulfur clusters called respectively F_X, F_A, and F_B.

Each photon energy hν absorbed by antenna's pigment networks made of predominantly chlorophyll molecules and few β-carotenoids in approximately 10^{-15} s. The absorbent energy excited peripheral pigment molecules, then the excitation energy migrates through internal pigments (e.g. resonance energy transfer), till they reach P_{700} site in the RC. Massive resonance energy harvested by chlorophyll special pair within the deep band gap and subsequently the work function difference between P_{700} and the first acceptor/donor site, A_{cc}, caused generation of the electron to transfer through ETCs [7,20].

Light-induced charge separation oxidizes the primary electron donor P_{700} chlorophylls *a*/a' heterodimer and A_{cc} site with redox potential (E_{RP}) of 430 mV, respectively. Then the second electron acceptor A_0 a chlorophyll monomer reduced (E_{RP} of −1000 mV), then the electron transferred to A_1 (E_{RP} of −800 mV) then to F_X (E_{RP} of −705 mV), F_A (E_{RP} of −520 mV) and finally F_B (E_{RP} of −580 mV) [8,9].

This novel photovoltaic function of PSI has been recently applied in different optoelectronic devices. For example, PSI deposited on various conducting and semi-conducting material substrates like Au [10–13], ITO [14], Graphene derivatives [15], and TiO_2 [16] for photocurrent generation purposes. The noteworthy approach toward fabricating a solid-state photovoltaic cell based on PSI is reported by Gordiichuk and co-workers [17]. There is a valuable review on PSI photovoltaics which maintains more detailed applications and records [18]. In this approach, our group previously has fabricated two different photovoltaic system based on PSI pigment-protein complex extracted from young spinach leaves, an electrolyte cell and a solid-state one, which prepares additionally a comparison situation. Here we report our latest solid-state bio-organic solar cell based on PSI pigment-protein complex.

2. Experimental

As shown in Fig. 1, the intended solar cell stack contains amino acidic substrate, PSI multi-layer, a rough and porous interlayer of fullerene-C60, Indium tin oxide (ITO) as the anode, and the cathode made of thin film of gold.

2.1. Isolation of PSI complex from spinach leaves

Preparation of PSI pigment-protein complex [19]. Fresh leaves of spinach (*Spinacia oleracea* L.) were purchased from the local market and then prechilled in the dark overnight. The leaves were homogenized in a buffer containing sucrose (0.3 M, Sigma-Aldrich, 99.5%), NaCl (15 mM, EMD Millipore) and tricine (30 mM, Sigma-Aldrich, 99%)–NaOH pH 7.8. The slurry was filtered through four layers of cheesecloth and centrifuged for 2 min at 2000 g. The resulting chloroplasts were washed twice in a hypotonic buffer containing EDTA (5 mM, Sigma-Aldrich) and 5 mM tricine–NaOH pH 7.8. Unstacked membranes were isolated by centrifugation at 25000*g* for 10 min and suspended in a buffer containing 0.3 M sucrose and 30 mM tricine–NaOH pH 7.8.

Spinach thylakoids containing 6 mg Chl. mL^{-1} were solubilized in Triton X-100 (4.8% w/v, EMD Millipore). After stirring for 15 min, the sample was centrifuged for 15 min at 15000 g. The complex was further purified by diethyl aminoethyl (DEAE)-cellulose (Merck Millipore) column chromatography with an elution buffer containing 20 mM tricine–NaOH pH 7.8, 0.03% DM. All steps were performed at 4^{oC} under dim light. The collected solutions from the column contain PSI complexes were then dialyzed.

2.2. Fullerene-C60 preparation

Fullerene-C60 (Sigma-Aldrich, 99.5%) in solution phase, for spin-coating, were prepared with toluene (EMD Millipore) as the initial solvent and deionized water as the second solvent. 2.8 mg/ml is the solubility of fullerene C60 in toluene [26]. The measured volume of toluene was added to 4 mg C60 powder. After a few second of stirring, a solution with purplish color appeared, Fig. 2a. The solution was stirred on a magnetic stirrer in a beaker for about 20 min to reach a homogenized solution. Afterward, the amount of 40–50 ml deionized water was added to the system, Fig. 2b. After a while with respect to heating and using ultrasonic stirrer, toluene was evaporated and the fullerene-C60 was dispersed in deionized water made a brownish solution. The final solution were filtered through filter paper (Whatman 25 mm) to lose large aggregates. Fig. 2c.

2.3. Tyrosine amino acid

Suspension of tyrosine (L-Tyrosine, Sigma-Aldrich, 99%) in deionized water, for dip-coating, were prepared with just deionized water as the solvent. The precise amount of tyrosine (depend on intended area of coating) powder were added to deionized water. The complex was stirred well to minimize the size of tyrosine needles.

2.4. Bio-organic solar cell fabrication

Prior to device fabrication, the ITO-coated glasses (Sheet resistivity of 100 Ω/sq) were cleaned with the standard procedure using distilled water, acetone, and isopropanol. The substrates were then masked with plastic tapes and treated with UV/O3 for 10 min, respectively. The masked substrates were dipped in activated tyrosine suspension and rest for 2 days. Afterward, the samples were pulled out carefully and dried under clean-desk atmosphere. Deposited layer of tyrosine was soaked gently in deionized water to remove any unbounded colloids. After a mild drying processing, the solution containing PSI were deposited through spin-coating. In the next step, fullerene-C60 were deposited through spin-coating, subsequently. The samples were transferred to a sputtering machine contains gold cathode. Finally, the device were finished with 30–40 nm layer of gold deposited via sputtering under the condition of 150 mbar for about 300 s. The masks were carefully rejected and cells with the active area of 50 mm^2 were obtained.

2.5. Characterization

Device performance measurements were done using solar simulator contains metal halide lamp of AM 1.5G spectrum with 80 $mWcmm^{-2}$ calibration. Cross section and surface morphologies of the layers were studied by scanning electron microscopy (SEM, Tescan Vega/II). Hitachi-CF16RX and SigmaII-3-30 K centrifuge machines were used during protein extraction. Spectrophotometric characterizations were recorded via both UV–Vis Carry 100 Bio and ELIZA power wave xs2.

3. Results and discussions

Although this quest provides advancements in organic-based