Integration and modification of photosystem I for bio-photovoltaics
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In the previous chapter, PSI was incorporated into a BHJ solar cell to determine the dipole of PSI and to measure the average orientation of the protein complex. Here, PSI was sandwiched between titanium oxide (TiO$_x$) and the optically-transparent hole-conducting polymer polytriarylamine (PTAA). In this solar cell device architecture, PSI acts as the sole active layer, resulting in a high open-circuit voltage of 0.76 V, a fill factor of 45% and a short-circuit current density of 2.9 mA/m$^2$. Our experiments demonstrate the functionality of PSI in a solid-state bio-photovoltaic device and that photoactive megadalton-protein complexes are capable to operate in a dry non-natural environment that is very different from the biological membrane.

4.1 Introduction

Photosynthesis can be a great inspiration for chemists and physicists to fabricate artificial light-energy conversion systems. To mimic light harvesting, as found in light harvesting complex II (LHC II), which were introduced in the first chapter, dendrimers were synthesized that contain donor and acceptor dyes distributed over the dendritic scaffold1, 2. Besides dendritic scaffolds, other structures were employed to host dye molecules in a light harvesting configuration like DNA3. While light harvesting has been reported with several scaffolding strategies, the oxygen evolving complex (OEC) that is found in Photosystem II is much harder to mimic with synthetic systems. An artificial OEC was formed that is composed of cobalt and phosphate4. From this material films were produced on surface of irradiated semiconducting materials like ZnO5. In such design, light absorption is combined with water splitting to achieve solar oxygen production.

Here, we aim for a different strategy of biomimetics. We take photoactive natural building blocks and let them perform their function in an artificial device. In this chapter, we combine the easy processing conditions of organic semiconductors and the formation of monolayers with a photoactive protein complex. As a result, a solid-state bio-organic solar cell was obtained with PSI as the only photoactive component. Another key component of this device was a polytriarylamine polymer that is hole conducting and transparent in the visible where light absorption of PSI occurs. Moreover, special attention is paid to the compatibility of PSI with organic solvents during device fabrication and an alternative method is presented to avoid contact of the biological component with organic solvents.

4.2 Integration of PSI inside solid-state solar cells

Similar as for the preparation of a BHJ, a PSI layer needs to be installed on the electrode. The directing linker molecule dihydroxyacetone phosphate was immobilized on titanium suboxide (TiOx, x=1, 2) supported on glass substrates.6 The self-assembled monolayers on the metal oxide surfaces were immersed in a PSI solution as described in the previous Chapter 3 for ITO. Afterwards, they were studied with the help of AFM to determine the surface coverage. On TiOx an average number of $1.7 \times 10^{15}$ m$^{-2}$ PSI monomers corresponding to a surface coverage of 50% was found allowed recording of an absorption spectrum of a PSI monolayer assembled on the transparent substrates under dry conditions. Characteristic absorption peaks of PSI were detected at 430 and 660 nm and the shape of the spectrum resembles the absorption behaviour of PSI in solution (Figure 4.1a). Such absorption measurements indicate that the dihydroxyacetone phosphate linker is well suited for incorporation of PSI by binding to the TiOx surfaces, which is interacting with the PSI by electrostatic and hydrogen bonds.
With knowing the dominant orientation of PSI on the metal-oxide substrate (Chapter 3), the fabrication of solid-state solar cells with PSI acting as the active layer for photo-current generation was realized. For these devices, two major modifications were introduced in relation to the cells described in Chapter 3. First, TiO\textsubscript{X} was placed on the ITO surface because of its electron-selective properties and its transparency. Second, the blend consisting of MEH-PPV and PCBM covering the PSI layer was replaced by a semiconducting polytriarylamine polymer (PTAA). This polymer was chosen because it is transparent to light in the visible region and therefore does not interfere with the major long-wavelength absorption of PSI.\textsuperscript{8} PTAA was introduced as a layer on top of PSI by spin coating it from chlorobenzene solution. The energy diagram of fabricated device is described in Figure 4.1b.

The overall device structure is schematically depicted in Figure 4.2a and the device function is anticipated as follows: PSI absorbs light and generates electrons that are transported via the TiO\textsubscript{X} layer to the ITO bottom electrode. At the same time, the generated holes are transported through the p-conducting PTAA layer to the MoO\textsubscript{3}/Al top electrode. Figure 4.2b shows the current density-voltage characteristics of the biophotovoltaic device under illumination of simulated AM 1.5 sunlight, with an intensity of 1 Sun. To exclude absorption and subsequent photo-generation of charge carriers by the titanium oxide and PTAA, a 435 nm long pass filter was employed. A clear photovoltaic response was obtained under standard solar-cell testing conditions, which can be attributed to photocurrent generation by PSI. The activity of PSI in this solid-state device is undoubtedly confirmed by photocurrent action spectra. A peak between 600 and 700 nm was observed, which coincides with the absorption of PSI. Figure 4.3a. A reference device without the PSI monolayer gave no response in this wavelength region. For further characterization of the PSI bio-photovoltaic cell, the \textit{J-V} curves were analysed (Figure 4.2b-c), which was not done in previous studies.\textsuperscript{9-15} The device exhibited an impressive open-circuit voltage of 0.76 V, retaining...
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A large part of the intrinsic energy-level potential of PSI. Furthermore, a fill factor of 45% was measured. The short-circuit current is low, which can be mainly attributed to the weak light absorption of the thin PSI monolayer. In addition, the energy levels of the hole- and electron-transport layers (PTAA and TiO_x) are not fully aligned with the energy levels of PSI, which may limit charge extraction. To initially test the stability of such a device, we performed three measurements within one week. It can be clearly seen that the PSI is stable for this period of time in the dry environment (Figure 4.3b). No decrease in short-circuit current density was observed.

Figure 4.2. (a) Current density-voltage plots of solar cells with PSI as active layer sandwiched between TiO_x and PTAA, in dark (black) and under simulated sunlight with an intensity of 1000 W/m^2, 1 Sun (red). (b) The result on a semi logarithmic scale. A 435 nm long pass filter was employed to exclude photo-generation due to PTAA and TiO_x, which absorb light in the UV-region.
Figure 4.3. (a) External quantum efficiency (EQE) of a device with and without PSI as active layer between TiO$_x$ and PTAA. (b) Time-depended stability study of PSI fabricated solid-state cells.

Figure 4.4. Effect of chlorobenzene (CB) treatment on the external quantum efficiency of PSI photovoltaic devices with a TiO$_x$ electron-transporting layer and a PTAA hole-transporting layer. (a) Response of PSI (in the 600-700 nm region) decreases with increasing number of CB washing steps. (b) The response in the short-wavelength region increases with increasing number of CB washing steps. The response in this region is due to charge generation at the TiO$_x$/PTAA interface. This indicates that a certain amount of PSI complexes is removed upon each CB washing step, resulting in a larger contact area between TiO$_x$ and PTAA.

Again, special attention was paid to the effects of the organic solvent processing on the PSI layer. For the preparation of control devices, the PSI monolayer deposited on the TiO$_x$ was repeatedly washed with chlorobenzene before spin-coating PTAA. An increasing number of washing steps that accompanies a gradual decrease in the external quantum efficiency (EQE) indicates that chlorophyll a is not liberated from PSI, pigment absorption does not occur on TiO$_x$, and that
charge generation originates exclusively from the intact photosynthetic protein complex (Figure 4.4a). Instead, the decrease in EQE can be attributed to a gradual removal of PSI complexes from the TiO\textsubscript{x} surface with repeating chlorobenzene washing steps and shows increase in the current caused by formation of direct contact with TiO\textsubscript{x} surface (Figure 4.4b). On a gold surface, loss of PSI molecules upon washing with chlorobenzene was also observed in Chapter 3.

### 4.3 Lamination of PTAA on PSI monolayer

In the above paragraph, special attention was paid to demonstrate that the processing conditions of organic electronic devices, especially spin coating of a top layer onto PSI layer employing organic solvent does not harm the protein component. In this paragraph, we add another control experiment that also represents a bio-electronic device fabrication procedure that fully avoids contact between organic solvent and the biological moieties. Therefore, the hole conducting polymer PTAA was spin coated onto a glass surface, which was subsequently lift-off by slow dipping of the substrate with polymer inside deionized water. The release of the PTAA layer was due to water penetration between polymer and glass surface. Next, the floated polymer film was transferred on top of an ITO/TiO\textsubscript{x}/PSI substrate and dried. This fabrication technique ensures that PSI is not exposed to any organic solvent. The devices are finished by evaporation of a MoO\textsubscript{3}/Al top contact. The measured $J$-$V$ characteristics, as presented in the Figure 4.5, are very similar to the characteristics of devices prepared by directly spin coating the PTAA layer on top of the PSI monolayer employing chlorobenzene as solvent. Therefore, we conclude that the photovoltaic response of our devices is due to the intact proteins and not due to leached chlorophylls. An electrical current of 2.1 mA/m\textsuperscript{2} and a $V_{OC}$ of 0.7 V were measured.

![Figure 4.5. Current density-voltage characteristics in dark (black line) and under illumination (red line) of a PSI solar cell with a laminated PTAA hole-transport layer.](image)

The measured performance of a single layer of PSI inside solid-state solar cells is lower than the possible theoretical limit\textsuperscript{16}, which can be due to misalignment of energy levels of P700 reaction.
center and the used PTAA hole conducting polymer, which can cause efficient hole extraction from PSI. Also limitations can be due to not perfect orientation of PSI proteins and bad contacts between the high molecular weight polymer and PSI protein that differ significantly in their polarities.

4.4 Conclusions

In this chapter, it was demonstrated that a biological component consisting of the photoactive protein complex PSI can be combined with an organic semiconducting material, the hole conductor polytriarylamine to form an all-solid state biophotovoltaic cell. Thereby, both compounds maintain their original optoelectronic properties. Two ways of fabricating such devices are presented. In the first one, a PSI monolayer installed on an electrode surface is spin coated with the semiconductor polymer from the organic solvent. In the second one, contact between the organic solvent and the biological moiety is completely avoided. This is achieved by producing a free standing semiconducting polymer layer and laminating it on the PSI monolayer. The resulting devices were characterized by a large open-circuit voltage and a photocurrent action spectrum exhibiting the typical absorption features of PSI. These successful proof-of-concept studies will fuel further activities of exploiting new material combinations of bioorganic hybrids for solar power generation.

4.5 Methods

**PSI immobilization on TiO$_x$ surfaces and absorption spectrum measurements:** TiO$_x$ surface were immersed overnight (14 hours) in 1 mM solution of dihydroxyacetone phosphate hemimagnesium salt hydrate in deionized (DI) water. After washing the surfaces with DI water and drying with a flow of nitrogen, the substrates were ready for formation of PSI monolayers. Therefore, PSI stock solution was diluted twice with Buffer A and the substrates were incubated for 2 hours with this solution in the dark. After the immobilization, PSI substrates were rinsed with DI water and dried with a nitrogen flow. ITO and TiO$_x$ substrates equipped with a PSI layer were used for device preparation. Absorption spectra of PSI monolayers were recorded with a Jasco V-630 spectrophotometer at 25°C under dry conditions. PSI ITO substrates were used for atomic force microscope (AFM) investigations and to assess the protein coverage.

**Preparation of TiO$_x$ layers:** TiO$_x$ layers were obtained by spin coating of a 1 wt.% solution of titanium isopropoxide in isopropyl alcohol. The layers were converted to TiO$_x$ by hydrolysis in air for 1 hour and were subsequently annealed at 150°C for 10 min to obtain layers of ~5 nm.

**Fabrication of photovoltaic device:** Glass substrates, pre-patterned with indium tin oxide, were thoroughly cleaned by washing with detergent solution, ultrasonication in acetone and isopropyl
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alcohol, followed by UV-ozone treatment. For the PTAA-based cells, the cleaned substrates were coated with a TiO_x layer, followed by self-assembly of a PSI monolayer. Subsequently, a 90 nm PTAA layer was spun from a chlorobenzene solution in a nitrogen-filled glovebox. The devices were finished by thermal evaporation of a MoO_3(10 nm)/Al(100 nm) top electrode at a base pressure of 1×10^{-6} mbar.

Device characterization: Electrical measurements were conducted in a controlled nitrogen atmosphere in the dark and under illumination of a Steuernagel Solar Constant 1200 metal halide lamp, which was set to 1 Sun intensity using a silicon reference cell and correcting for spectral mismatch. EQE spectra were recorded versus a silicon reference, using a custom-built setup comprising a lock-in amplifier, a transimpedance amplifier, and a focused, chopped monochromatic beam from a quartz tungsten halogen lamp, and a range of narrow band pass filters.
4.6 References


