Solar Cells

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Generation of Alternating Current in Response to Discontinuous Illumination by Photoelectrochemical Cells Based on Photosynthetic Proteins**

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There is developing interest in the device properties of nature's chlorophyll-containing photochemical reaction centers (RCs) driven by the need to establish a range of technologies for harvesting solar energy and the development of nanoscale electronic components and sensing materials.[1] These RCs operate as photodiodes, converting light energy into a linear or cyclic flow of electrons,[2] and at the heart of this biological function lies a light-induced separation of electrical charge. A much commented feature of natural RCs is that they operate with a quantum yield close to unity.[2] In addition to uses in photovoltaic devices[3] and light-powered fuel cells,[4] RCs have potential applications as photosensors,[5] phototransistors,[6] biosensors for detection of environmental pollutants.[7]

A variety of photoelectrochemical cells based on RCs have been constructed,[3] mostly comprising two or three electrodes with RCs adhered to a working electrode that is submerged in a buffer solution containing one or more redox mediators.[8–11] A number of linkers have been employed to achieve oriented adhesion of RCs to the electrode surface, and in many cases construction of the working electrode has required a complex, multistep fabrication procedure. Photocurrent densities between one and several hundred nA cm^{-2} have typically been obtained in response to red light of an intensity of a few tens of mW cm^{-2},[8,9] and a small number of studies have reported higher photocurrents in the μA or even mA range.[9–12]

Herein, protein photoelectrochemical cells were constructed using either RCs or RC–LH1 complexes from *Rhodobacter* (*Rba.*) *sphaeroides*. In the RC–LH1 complex a central RC is surrounded by a light harvesting 1 (LH1) pigment protein (the structures and mechanism of these complexes are described in Figures S1 and S2 in the Supporting Information). A very simple fabrication procedure was used in which a mixture of protein and the redox mediator *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (TMPD) was injected into an approximately 10 μL cavity formed between a fluorine-doped tin oxide (FTO) glass front electrode and a Pt-coated rear electrode (see the Supporting Information). The cells had an area of around 1 cm^2, and the absorbance spectra of the proteins within the cells were consistent with their spectra in detergent solution (Figure S3 in the Supporting Information). Cells were illuminated with white light passed through a 570 nm long-pass filter.

Illumination of a cell that was constructed using a mixture of RC–LH1 complexes and TMPD produced a short-circuit current density (J_{SC}) that stabilized at a value of 0.15 μA cm^{-2} after approximately 20 s (Figure 1a); the direction of the current indicates electron flow into the cell cavity from the FTO-glass front electrode. The initial spike of current flow was similar to a feature that has been seen in photoelectric measurements on RCs in planar lipid bilayers[13] and Langmuir Blodgett films.[14] The initial spike was consistently seen in multiple cells, and its origins are considered below. The open-circuit voltage (V_{OC}) of the RC–LH1 cell also showed an initial small spike (Figure 1b), settling over the next approximately 20 s to a steady value of around 7 mV. Experiments with monochromatic excitation showed that the external quantum efficiency (EQE) of the RC–LH1 cell had a maximum of 0.95% at 875 nm (Figure 1c), and the shape of the EQE action spectrum matched that of the absorbance spectrum of the RC–LH1 complex in solution (Figure 1c). This matching spectrum confirmed that the photocurrent was dependent on photochemistry catalyzed by the RC after harvesting of photons by the pigments of the RC and the surrounding LH1 antenna. No currents were seen in the absence of RC–LH1 complexes (Figure 1a, blue). Similar data were obtained on cells that had been constructed using purified RCs (stable J_{SC} of ca. 0.1 μA cm^{-2}, initial spike of ca. 0.6 μA cm^{-2}), but the maximum EQE was somewhat lower at 0.115% (see Figure S4 in the Supporting Information).

These photocurrents were observed despite the fact that no special steps were taken to bind or orient the protein component at either electrode, a major concern of most previous studies.[8] Moreover, only a single redox mediator, TMPD, was used in the present work. In all RC-based photovoltaic setups described previously, different mediators or processes have been used to deliver electrons to the photo-oxidized primary electron donor (P^+) at the "P-side" of the RC and remove electrons from the photo-reduced acceptor quinone (Q_B^-) at the "Q-side" (see Figure S1 in the Support-

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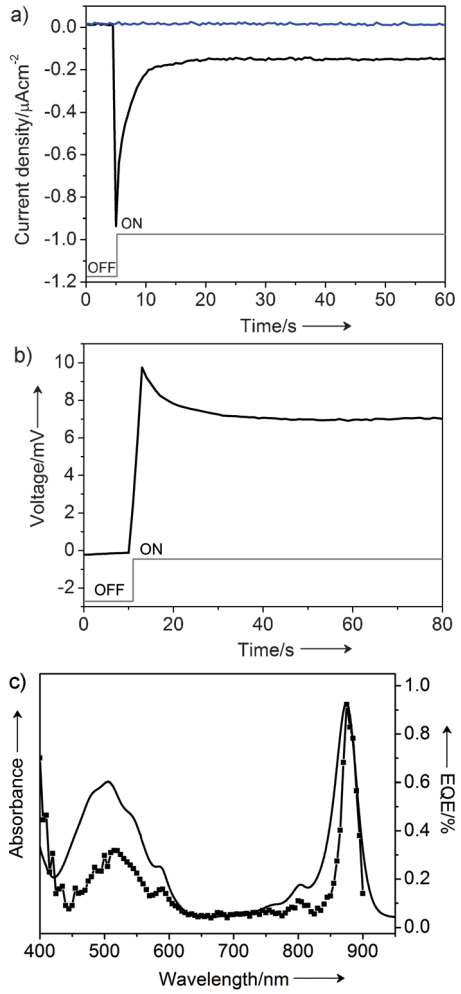

Figure 1. a) J_{SC} output by a cell with RC–LH1 and TMPD (RC–LH1 cell; black) and a control cell with only TMPD (blue) under continuous illumination, indicated by the gray bar. b) V_{OC} of the same cell in response to illumination. c) Action spectrum of EQE (squares/lines) compared to the solution absorbance spectrum of the RC–LH1 complex (line).

ing Information). In the present case, it is well-known that TMPD is an efficient reductant of P^+, and that $TMPD^+$ can act as an oxidant of Q_B^-.[15] However, if the RCs and TMPD in the present cell were simply free to interact in solution, one might expect any $TMPD^+$ formed by reduction of P^+ to be re-reduced by Q_B^- in a futile internal redox cycle. The fact that a photocurrent was seen implied that, at least for a fraction of the proteins in the cell, the process that delivered electrons to P^+ from the FTO-glass electrode must have been separated from the process that delivered electrons from Q_B^- to the Pt electrode. This separation of the two processes suggested oriented adherence of RC–LH1 or RC complexes to one or the other electrode, and to investigate the relative likelihood of this the contact angle formed by a drop of deionized water placed on either electrode was measured (Figure S5 in the Supporting Information). The obtained values showed that the FTO glass had a hydrophilic surface (18.7°), whereas the Pt surface was hydrophobic (93.8°), thus suggesting that the photoactive proteins would be more likely to attach to the (electron-injecting) FTO-glass front electrode.

Taking this result into account, along with the vacuum potentials of the different components, Figure 2 shows a schematic that accounts for the photocurrent output of these protein-based cells. The photoactive fraction of RC (or

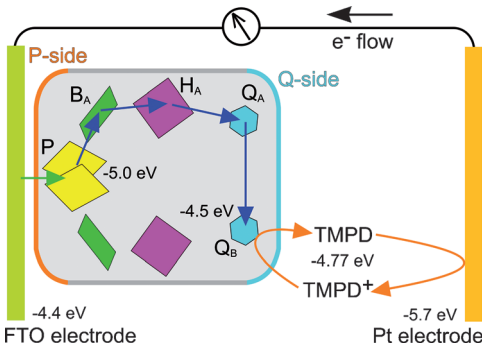

Figure 2. Proposed mechanism for operation of the RC and RC–LH1 cells with TMPD as the single redox mediator. Current-supporting RCs (as shown) or RC–LH1 complexes (not shown) are oriented with the P-side close to the FTO-glass electrode. Arrows indicate the route of electron transfer through the RC (blue), through the TMPD/$TMPD^+$ pool to the Pt electrode (orange) and into the P-side of the RC from the FTO-glass electrode (green). Electron transfer within the RC from the P bacteriochlorophyll dimer to the Q_B quinone occurs via a monomeric bacteriochlorophyll (B_A), bacteriopheophytin (H_A), and quinone (Q_A).

RC–LH1) complexes are proposed to be oriented with their P-side close to the FTO-glass electrode. After photo-induced charge separation in the RC (blue arrows), P^+ is either re-reduced directly by the FTO (green arrow), or by an intermediary small pool of TMPD/$TMPD^+$ that is out-of-equilibrium with the TMPD in the bulk phase (for simplicity only the former arrangement is referred to below and shown in Figure 2, but further experiments will be required to clarify this point). Current flow is completed by $TMPD^+$ in the bulk phase of the cell, which oxidizes Q_B^- and shuttles electrons to the Pt electrode (orange arrows).

Exposure of these protein photoelectrochemical cells to one or more light-on/light-off cycles produced an unexpected result. In previous reports the RC-dependent photocurrent has been observed to rapidly drop to zero when illumination was terminated.[8,9,11] To our surprise, in the present case turning the actinic light off consistently produced a very rapid switch to a transient reverse current (Figure 3a), which decayed to zero over approximately 20 seconds. This response was seen during multiple light-on/light-off cycles for both RC and RC–LH1 cells (see Figure S6a,b in the Supporting Information), and this alternating current (AC) behavior could be emphasized by modulating the actinic light at a faster rate in both types of cell (shown for an RC cell in Figure 3b). As expected, the V_{OC} of these cells also reversed polarity in response to light-on/light-off cycles (shown for an RC–LH1 cell in Figure S6c in the Supporting Information). This alternating current output was not seen in cells containing TMPD electrolyte but lacking RC (Figure 3b, blue).

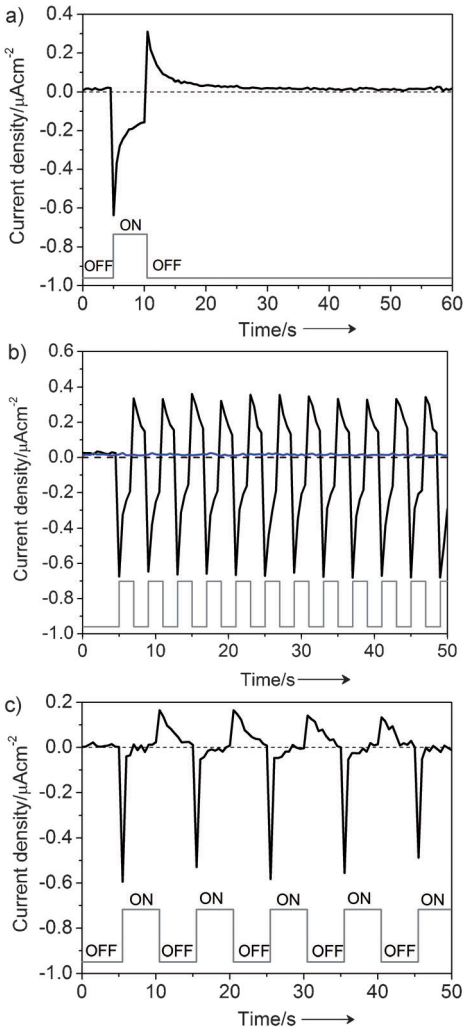

Figure 3. a) J_{SC} output by an RC cell in response to a single 5 s period of illumination (gray bar). b) J_{SC} of a cell with RC and TMPD (RC cell; black) and a control cell with only TMPD (blue) in response to 2 s light-on/light-off cycles. c) J_{SC} of an RC cell in the presence of stigmatellin (1.8 mM), exposed to multiple 5 s light-on/light-off cycles.

What could be the source of the AC output seen in response to modulated light intensity? A known feature of the RC is that, under conditions of illumination where external reduction of P^+ is rapid relative to external oxidation of the quinones, the multiple quinone, bacteriopheophytin (BPhe), monomeric bacteriochlorophyll (BChl), and dimeric BChl cofactors of the RC can each undergo reduction.[16] As a result, under conditions where electron flux into the P-side of the RC is faster than electron efflux from the Q-side, there is the possibility that all six monomeric cofactors of the RC could act as a sink for electrons. In the present study it was found that the redox mediator used, TMPD, was capable of supporting a sizeable direct photocurrent. However it has been reported that the rate of Q_B^- oxidation by $TMPD^+$ is some 2400-fold slower than reduction of P^+ by TMPD,[15a] and so it is conceivable that the former reaction could constitute a kinetic bottleneck.

Given this difference in reduction and oxidation rates, we propose that the spike of forward current seen on illumination of the RC-based cell is due to a kinetic limitation at the Q-side of the RC that produces an accumulation of negative charge by the multiple cofactors of the RC, balanced by an over-oxidation of the bulk $TMPD^+$/TMPD redox mediator. This kinetic imbalance leads to an accumulation of charge inside the RC that declines from its initial maximal value as further reduction of the RC cofactors becomes energetically less favorable. After 10 seconds or so the capacity of the RC for "stored" electrons becomes full and a steady-state condition is reached; in this steady state the amount of RC-dependent direct current (DC) flowing through the cell is limited by the rate of electron flow from the quinones of the RC to the Pt electrode, mediated by the bulk pool of $TMPD^+$/TMPD (Figure 4a). Immediately after the light is turned off (Figure 4b), photochemical charge separation and the DC output of the cell cease, and the potential difference between RC

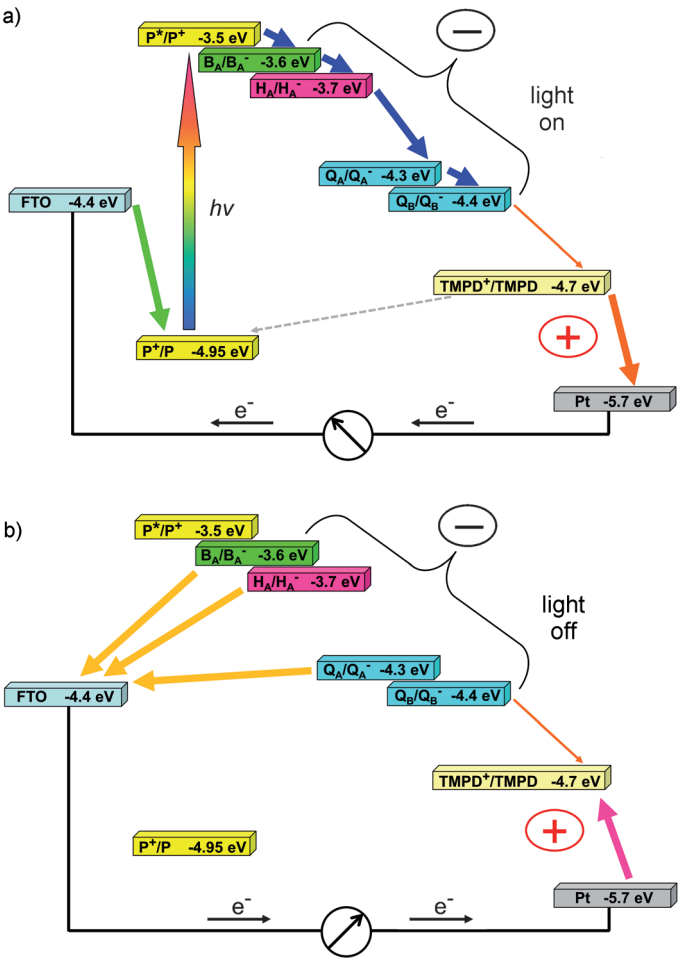

Figure 4. a) Proposed mechanism of current generation in the light. Photoexcitation in the RC (rainbow arrow) initiates charge separation in the RC (blue arrows); electrons are shuttled to the Pt electrode by TMPD (orange arrows); P^+ is reduced by the FTO-glass electrode (green arrow); limiting electron transfer from the RC to $TMPD^+$ (narrow orange arrow) causes an initial over-reduction of the RC cofactors and over-oxidation of the TMPD pool. b) Proposed mechanism of reverse electron flow after turning off the excitation light. Electrons are donated by the over-reduced RC cofactors to the FTO electrode (gold arrows), and the $TMPD^+$ pool is reduced by the Pt electrode (magenta arrow), thereby producing a transient reverse electron transfer until the potential difference is dissipated.

cofactor "compartment" and the $TMPD^+$/TMPD "compartment" drives electron flow between the two. The fact that a reverse current is seen indicates that re-equilibration of the system via the external circuit is more favorable than internal re-equilibration owing to direct oxidation of the RC quinones by $TMPD^+$.

A prediction of this mechanism is that prevention of electron flow through the Q_B site of the RC should abolish the DC output, but the AC component should be retained. This component should be retained, because the light-powered accumulation of a potential difference between the current-generating RCs and the bulk $TMPD^+$/TMPD pool and dissipation of this difference in the dark through the external circuit would be expected to still take place even when the Q_B site is blocked by an inhibitor.

Addition of the Q_B-site inhibitor stigmatellin[17] to the RC cell produced data consistent with this prediction. The light-dependent DC component was abolished in the presence of stigmatellin (Figure 3c), but the AC component occurring in response to alternating light-on/light-off events was still seen, albeit with a modified initial amplitude and kinetics of decay.

In further support of the proposed mechanism, it was found that inclusion of a 30-fold molar excess of water-soluble ubiquinone in the electrolyte in addition to TMPD enhanced the DC output of the cell to around 1.8 $\mu A\,cm^{-2}$ for an RC–LH1 cell and the AC component was abolished (Figure S7a and S7b, respectively, in the Supporting Information). Water-soluble quinone would be expected to improve electron flux from the Q_B site of the RC to the counter electrode, thereby enhancing the generation of DC. At the same time the improvement of this electron flux by the water-soluble quinone would work against the development of the potential difference between the RC compartment and the bulk electrolyte compartment that is responsible for driving reverse electron flow, thereby diminishing or abolishing the generation of AC. Other possible origins for the dark reverse current were also considered, but the mechanism proposed here provided the simplest explanation that fitted with known properties of the RC and electrolyte, and was in accord with a more extensive set of data that will be published elsewhere.

In relative terms the magnitude of the J_{SC} output obtained under continuous illumination from the cells described above was very low compared to those obtained from conventional silicon or dye-based solar cells.[18] However there is ample scope for improvement of the current density. For example, the present device uses an essentially planar electrode of minimal surface area. However, a feature of the most efficient dye-sensitized or polymer-blend solar cells[19] is a complex nanostructure that provides an extensive interfacial area at which the initial charge separation is conducted. In principle it should be possible to interface RCs with a nanostructured electrode with a much larger surface area, and so increase the current density output of the cell.

The data described above provide proof of principle for a novel AC output from a photoelectrochemical cell under modulated light conditions. The fundamental mechanism is essentially that of a solar-powered capacitor that charges over a period of time during the light-on phase and discharges through the external circuit over a similar period after switching the light off, and in the case of the protein cells described above this is achieved through a single nanoscale component with integrated photovoltaic and capacitive properties. We are currently working towards achieving a more symmetrical reverse current to further explore this concept, as well as examining the use of different electrode materials, alternative redox mediators, engineered photovoltaic proteins, modified fabrication procedures, and alternative means of modulating the incident light intensity to maximize the AC output of these protein cells.

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