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Picosecond Electron Transfer from Photosynthetic Reaction Center Protein to GaAs

Lior Sepunaru,[†] Irena Tsimberov,[‡] Ludmila Forolov,[†] Chanoch Carmeli,[†] Itai Carmeli,[*,§] and Yossi Rosenwaks[*,‡]

Department of Biochemistry, School of Electrical Engineering, and School of Chemistry and the Institute for NanoScience and Nanotechnology, Tel Aviv University, Tel Aviv 69978, Israel

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ABSTRACT

An extremely fast electron transfer through an electronically coupled junction between covalently bound oriented photosynthetic reaction center protein photosystem I (PS I) and n-GaAs was measured by time-resolved photoluminescence. It was found that the n-GaAs band edge luminescence intensity increased by a factor of 2, and the fast exponential decay constant was increased by a factor of 2.6 following the PS I self-assembly. We attribute this to picosecond electron transfer from the PS I to the n-GaAs surface states.

The use of biological proteins in solid-state electronics is intriguing because proteins were perfected over hundreds of millions of years of evolution to become highly efficient catalysts. The use of genetic engineering and nanotechnologies enabled the function of some proteins in a dry environment that is hostile to living organisms. Of special interest are the efficient photoactive photosynthetic proteins that can serve in photosensing applications and have potential use in the growing field of nanoelectronics and solar energy conversion. We have used photosystem I (PS I) protein derived from cyanobacterial membrane owing to its robustness and outstanding photoelectronic properties. The photoactive reaction center PS I is a nanosized protein−chlorophyll complex that harvests photons with a quantum efficiency of ∼1 and generates a photopotential of 1 V across a 9 nm protein[1,2] and is functional in a dry environment.[3,4] In cyanobacteria, the complex consists of 12 polypeptides, some of which bind 96 light-harvesting chlorophyll and 22 carotenoid pigment molecules. The electron transport chain in PS I contains a special pair of chlorophyll *a* (P700) that transfer electrons following photoexcitation in 1 ps to a monomeric chlorophyll *a* (Chl), through two intermediate phylloquinones (PQ) and three [4Fe−4S] iron sulfur centers (FeS), the final acceptors that are reduced in 0.25 μs. PS I was also found to be photoactive when covalently bound to metal surface[5] and to nanotubes.[6] In earlier works, fabrication of active semiconductor/protein interfaces under dry[7,8] and aqueous[9,10] environments were attempted. We have recently fabricated stable, dry, and functional junctions between PS I and GaAs[11] by covalently binding genetically engineered unique cysteine mutants of PS I to a chemisorbed monolayer of small connecting molecules on the semiconductors surfaces. Such dry junctions, stable for months in our laboratory environment, resulted in large photovoltages of 0.3 V and −0.47 V in PS I-coated p- and n-type GaAs, respectively. It was suggested that the negative photovoltage was a result of electron transfer from PS I to the semiconductor enhanced by an almost −0.9 eV difference between the n-GaAs band energy relative to the excited reaction center in PS I. The electron transfer to the semiconductor is taken as evidence that an electronically coupled junction was formed at the n-GaAs/PS I interface. In the present work the electron transfer dynamics between the PS I and GaAs was studied using time-resolved photoluminescence (TRPL) measurements of the hybrid junction. It was found that the n-GaAs band edge luminescence intensity increased by a factor of 2, and the fast exponential decay time constant increased by a factor of 2.6; we attribute this to picosecond electron transfer from the PS I to the n-GaAs surface states.

Band edge photoluminescence in direct gap semiconductors is due to recombination of electrons and holes at the surface and in the bulk. Consequently, the PL intensity and decay rate are determined by the carrier concentration and, therefore, can be used for monitoring charge transfer between

* Corresponding authors: Yossi Rosenwaks, tel +972-3-6406248, fax +972-3-6423508, e-mail yossir@eng.tau.ac.il; Itai Carmeli, tel +972-3-6405714, fax +972-3-640612, e-mail itai@post.tau.ac.il.

[†] Department of Biochemistry.

[‡] School of Electrical Engineering.

[§] School of Chemistry and the Institute for NanoScience and Nanotechnology.

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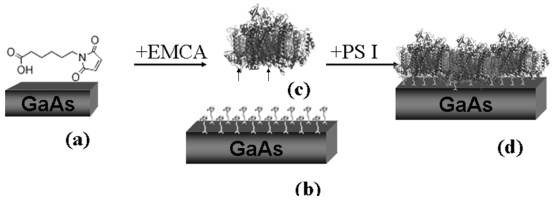

Figure 1. Schematic presentation of GaAs/PS I hybrid junction preparation. EMCA molecules are chemisorbed through the carboxyls on etched n- and p-GaAs (a, b). PS I modeled in a polypeptide backboned structure with cysteine mutants D236C/Y635C (space fill, black arrow) (c) are self-assembled as an oriented monolayer by covalent binding between the cysteine thiols and the EMCA maleimide moiety (d). The images of the PS I modeled by Pymol software from the coordinates of PDB 1JB0 file.

PS I and the semiconductor. The TRPL measurements were conducted on a self-assembled oriented monolayer of PS I on GaAs surface. An oriented PS I monolayer was fabricated by binding of the proteins to a monolayer of *N*-ε-maleimidocaproic acid (EMCA) linker molecules (Figure 1) which was chemisorbed to the etched n- and p-type GaAs through their carboxyl end as previously described.[11] The maleimide moiety of EMCA readily reacted with the mutated cysteines D235C/Y634C of PS I to form a dense oriented monolayer of PS I under aqueous conditions at 25 °C. The monolayer was dried under nitrogen.

The TRPL of the GaAs/PS I junction was measured using a previously described setup[12] in which a continuous wave diode-pumped Nd:YAG laser (Verdi Coherent Inc.) pumps a Ti-sapphire (Tsunami, Spectra Physics Inc.) laser, which provides high pulse repetition frequency (prf) of short pulses with full width at half-maximum (fwhm) of about 1.1 ps. The laser frequency was reduced using a pulse picker (model 3980, Spectra Physics, Inc.) to rates of 4 MHz or 800 kHz. The laser beam (wavelength of 808 nm or 404 nm) was focused on the sample surface, and the PL signal emitted from the sample was collected by a combination of a subtractive monochromator, a cooled multichannel plate photomultiplier (Hamamatsu R3809), and a time-correlated single-photon counting (TCSPC) system. The overall instrument response fwhm is around 35 ps (Figure 2a.1). The intensity and dynamics of the photoluminescence were measured at 870 nm (GaAs band gap).

Figure 2 shows the PL measured at a prf of 4 MHz (a) and 0.8 MHz (b) at 404 nm excitation wavelength which is absorbed by both the GaAs and the PS I. The PL was measured before (2) and following (4) the assembly of the PS I monolayers. The luminescence decays were analyzed using a biexponential fit which is an approximation for the surface (fast component) and bulk (slow component) recombination in the GaAs semiconductor.[13] The two decay time constants were determined by convolution of the PL transients using

$$I_{PL}(t) = \int_0^t E(t')R(t - t')\,dt'$$

where $I_{PL}(t)$ is the time-dependent PL intensity, $E(t)$ is the measured instrumental response function, and $R(t)$ is the biexponential function. Although more rigorous and accurate analyses of PL decay have been formulated and used by us

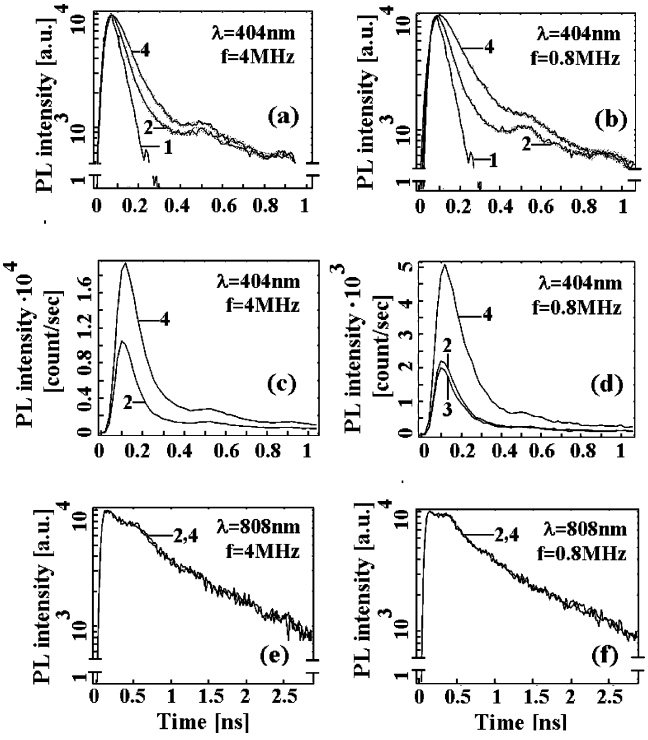

Figure 2. Time-resolved PL at 870 nm of PS I monolayer on n-GaAs. The PL intensities were measured in samples of n-GaAs substrate (2), n-GaAs/EMCA (3), and n-GaAs/EMCA/PS I (4). The samples were illuminated at 404 nm (a, b, c, and d) and at 808 nm (e, f) with laser flashes at a frequencies of 0.8 MHz (b, d, f) and 4 MHz (a, c, e) and counts were collected for 5 min (c, d). The normalized PL intensity rise and decay of n-GaAs substrate (2) and of n-GaAs/EMCA/PS I (4) were fitted to the biexponential equation and are shown relative to the system response of ~35 ps (1). PL intensity is given in arbitrary units (a.u.).

in the past,[14] the biexponential fit is sufficient to demonstrate the fast ET across the n-GaAs/PS I junction. At an excitation frequency of 4 MHz there was an increase in the fast component of the PL decay from 29 to 48.9 ps for n-GaAs and n-GaAs/PS I, respectively (Table 1). Yet, a bigger increase in the decay time constant of the n-GaAs/PS I sample (73.4 ps) was observed when the prf was decreased from 4 to 0.8 MHz. When the samples were excited at 808 nm, where only the GaAs absorbs the laser radiation (Table 1), no change in the PL decay rate was observed (Figure 2e,f). It is therefore suggested (see the discussion below) that the change in the decay rate is due to transfer of electrons from the excited P700 in PS I (Figure 3) to n-GaAs. It is estimated that the electron transfer from PS I to GaAs occurs in a few picoseconds, within the risetime of the PL intensity (Figure 2c,d).

We argue that this charge transfer induces the observed increase in the PL fast time constant that is observed immediately after the maximum PL intensity is reached. The additional slow down in decay rate that results from the decrease in the prf indicates that the relaxation of the charges in this hybrid system occurred at a rate of around 0.8 MHz. Therefore, it is reasonable to deduce that the rate of the back transfer of electrons from the n-GaAs surface states to the PS I occurred on the microsecond time scale.

Table 1. Time-Resolved PL at 870 nm of PS I Monolayer on *n*-GaAs

	fast decay time constant (ps) and PL intensity (a.u.)[a]			
	404 nm		808 nm	
	4 MHz repetition rate	0.8 MHz repetition rate	4 MHz repetition rate	0.8 MHz repetition rate
n-GaAs	29 ± 10^{-3} (1.05×10^4)	$28 \pm 3 \times 10^{-4}$ (2.2×10^3)	620 ± 1 (1.8×10^3)	700 ± 1 (1×10^3)
n-GaAs/EMCA	$28 \pm 3 \times 10^{-4}$ (1×10^4)	$30 \pm 5 \times 10^{-4}$ (2×10^3)	600 ± 1 (1.8×10^3)	690 ± 1 (1×10^3)
n-GaAs/EMCA/PS I	49 ± 10^{-3} (1.9×10^4)	$73 \pm 1.2 \times 10^{-3}$ (5×10^3)	590 ± 1 (1.8×10^3)	690 ± 1 (1×10^3)

[a] Normalized PL intensity at 870 nm was measured following excitation by laser pulses of $\lambda = 404$ nm or $\lambda = 808$ nm at frequencies of 4 or 0.8 MHz. The results of the fast time constant component of the biexponential normalized PL intensity decay rates of untreated n-GaAs, n-GaAs coated with a EMCA molecules (n-GaAs/EMCA) and a monolayer of PS I on n-GaAs (n-GaAs/EMCA/PS I) are shown. The PL intensities are given in parentheses in arbitrary units (a.u.).

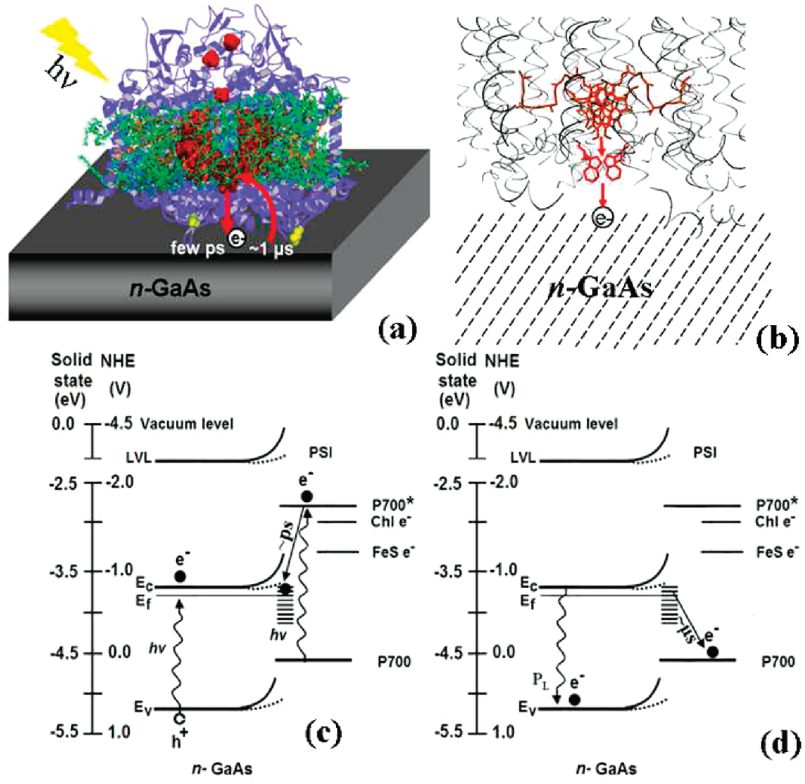

Figure 3. The molecular image and the scheme of energy levels of electron transport pathway between PS I and GaAs. (a) The molecular image of PS I indicates our conjecture for the electron pathways (red arrows) between PS I and n-GaAs. The image was modeled as a polypeptide backboned structure (blue), chlorophylls (green, rods), the electron transport carriers in red (space fill), cysteines D235C/Y634C in yellow (space fill). (b) The two tryptophans $W622_B$ and $W651_A$ that mediate electrons from the special chlorophyll pair P700 (red rods) to the semiconductor at the GaAs/PS I intersurface are shown. The images of the PS I modeled by Pymol software from the coordinates of PDB 1JB0 file. (c) Schematic presentation of energy levels in a n-GaAs/PS I junction indicating the light-induced charge separation generating an energy gap of 0.9 V that drives electrons from the exited P700* to the n-GaAs conducting band causing a decrease in the band banding. The primary and the final electron acceptors are Chl and FeS, respectively. (d) PL is emitted during charge recombination in the semiconductor and the extra electrons are recombined with the oxidized P700 during the relaxation of the system. The n-GaAs band energies and the PS I were determined as earlier described[11] and detailed in Supporting Information.

The time-integrated PL intensity increased by 1.8 and 2.3 when the PS I monolayer on n-GaAs was excited at a wavelength of 404 nm at repetition rates of 4 MHz (Figure 2c) and 0.8 MHz (Figure 2d), respectively. However, there was no increase in the PL intensity when a monolayer of only the linker molecule (EMCA) were adsorbed on the GaAs surface (Figure 2d) nor any increase in the PL intensity was observed at 808 nm (Figure 2e,f) where only the n-GaAs is excited. This can be explained as follows: the electron transfer from the PS I to the n-GaAs decreases the depletion type band bending of the GaAs and, consequently, the width of the n-GaAs surface space charge region resulting in an increase of the band edge PL intensity.[13,14] By comparing the relative amplitudes of the PL intensity of the n-GaAs/PS I with that of the untreated n-GaAs, a change of 0.19 V in band bending caused by the electron transfer was calculated (see Supporting Information). This quite significant band bending change of n-GaAs was caused by charge transfer from the PS I monolayer directly to the n-GaAs surface states which changed the surface space charge electric field. From the band bending, a theoretical calculation of the numbers of electrons that were transferred from the PS I monolayer to the n-GaAs surface was extracted (see Supporting Information). The calculation yielded an electron transfer that is expected from an absorption by a dense PS I monolayer.

On the basis of these results we have constructed a qualitative one-dimensional energy model (Figure 3) for the electron transfer dynamics in the n-GaA/PS I junction. The laser pulses at 404 nm excite both the GaAs and PS I. The excited electrons in the P700* (the excited state of the primary electron donor in the reaction center) are transferred to the n-GaAs surface states because of the favorable energy levels of the two (Figure 3c). The transferred electrons negatively charge the surface states of the n-GaAs and leave the PS I positively charged. This induced interfacial electric field is opposite is sign to the electric field of the n-GaAs space charge region. Consequently, the n-GaAs band bending and space charge region width decrease, causing an increase of the fast PL decay time constant and intensity.[15,16] The electron transfer rate can be estimated for photosynthetic proteins[17] as

$$\log_{10} k_{et} = 13 - 0.6(R - 3.6) - 3.1(\Delta G + \lambda)^2/\lambda \quad (1)$$

where k (s^{-1}) is the electron transfer rate, R (Å) is the edge to edge distance, ΔG (eV) is the driving force, and λ (eV) is the reorganization energy. The ΔG and λ terms reflect the Gaussian dependence of the rate on a Marcus-like electron transfer driving force. The energy levels of the n-GaAs surface states and P700 are estimated as -3.8 and -4.58 eV, respectively.[11] On the basis of PS I crystal structure (PDB 1JB0 file) the edge-to-edge distance from the GaAs surface to the P700 was estimated to be ~15 Å. Using a reorganization energy of about 1 eV, we obtain an electron transfer rate $k_{et} = 1$ MHz. This naïve calculation agrees only with the back electron transfer from the n-GaAs surface states to P700 (Figure 3d).

However, the picosecond electron transfer from the P700* to n-GaAs surface states is about 5 orders of magnitude faster. This faster rate can only occur if the forward electron pathway is either shorter or has adequate energy overlap between the two subsystems. Careful examination of the PS I crystal structure reveals a much faster pathway for the forward electron transfer from the P700* to the GaAs surface. In the proposed pathway the electrons are mediated trough a tryptophan pair $W622_B$ and $W651_A$ (Figure 3b). The aromatic side chains of the tryptophans are better conductors of electrons because of their extensive π electron system.[18] These tryptophans were apparently selected by evolution to mediate electron from the natural electron donor plactocyanin to P700 in PS I. Indeed, electron transfer from plastocyanin to P700 in PS I was inhibited when $W622_B$ was mutated.[19] Assuming fast conductance through the 7 Å of the tryptophan's π ring system, a shorter distance of 8 Å through the rest of the conducting medium was recalculated for the forward electron transfer between P700 and the GaAs surface. With eq 1, a rate constant of $\tau = 30.2$ ps for the electron transfer was calculated assuming an energy gap of -0.9 eV (energy levels of -2.81 and -3.7 eV for P700* and the GaAs conduction band minimum, respectively) and an edge-to-edge distance of 8 Å between P700* and the n-GaAs surface. It is possible to envisage that the forward electrons will move rapidly through the highly conducting

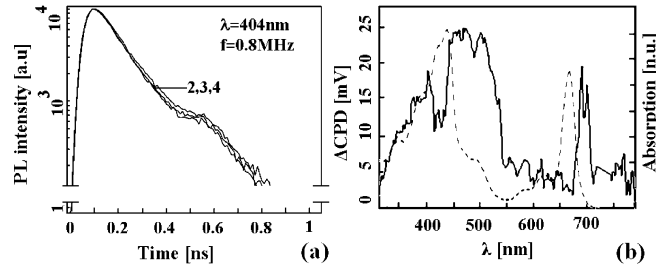

Figure 4. Time-resolved PL at 870 nm and SPS of PS I monolayer on p-GaAs. (a) Normalized PL intensity at 870 nm was measured following excitation by laser pulses of 404 nm at 0.8 MHz frequency. The normalized PL intensity rise and decay of p-GaAs (2), p-GaAs/EMCA (3), and of p-GaAs/EMCA/PS I (4) are shown. PL intensity is given in arbitrary units (a.u.). (b) The SPS results during continuous wave illumination of p-GaAs/EMCA/PS I after subtraction from the results of p-GaAs/EMCA (—) is compared to the absorption spectrum of PS I (---) in normalized absorption units (n.u.).

pathway and will be trapped as localized electrons in the n-GaAs surface states. The localized electrons may go down in energy and populate lower energy surface states within the GaAs band gap. These surface states might not be located directly underneath the PS I tryptophans. Therefore, the electrons will return through multitude of pathways in the protein from various locations on the GaAs surface to the $P700^+$ resulting in a slower backward than a forward electron transfer.

TRPL measurements of p-GaAs/PS I hybrid junctions showed no change in the PL decay rate when excited at wavelengths of 404 nm (Figure 4a) or 808 nm at different prf's. In addition, there was no increase in the PL intensity (data not shown) compared to the PL of the untreated p-GaAs. The integrated PL intensity measured for the p-GaAs was smaller by 1 order of magnitude relative to that measured for n-GaAs. This is evidence for a much stronger Fermi level pinning,[14] and therefore if there was an electron transfer from the PS I to the p-GaAs it would not induce a significant change in band bending. Moreover, there was a pronounced wavelength dependence of surface photovoltage spectrum (SPS) as shown by the measurements in Figure 4b. SPS measures changes in a semiconductor band bending induced by photogenerated carriers in the space charge region. The spectrum in Figure 4b was obtained by subtracting the measured p-GaAs/EMCA spectrum from that of p-GaAs/EMCA/PS I. There are two major photovoltage peaks at 470 and 688 nm which qualitatively resembles the absorption spectrum of PS I showed by the dashed line. The observed red shift and broadening in the SPS spectrum might be attributed to the effect of the p-GaAs space charge electric field on the chlorophyll absorption spectrum. The surface photovoltage is a result of electron transfer from P700 to the final acceptor (FeS) in PS I away from the interface between GaAs and the reaction center. This charge transfer increases the negative surface charge of the p-GaAs/PS I junction (Figure 1S in Supporting Information). Indeed, the displacement of negative charges to the surface of the PS I monolayer is not expected to cause a change in the TRPL decay rate as was observed for the p-GaAs/ PS I junction.

In summary, it was shown that the hybrid n-GaAs/PS I junction mediates a fast electron transfer from the exited reaction center (P700*) or the primary electron acceptor (Chl) (Figure 3) to the semiconductor surface. The electron transfer pathway in the n-GaAs/PS I junction was shown to be opposite to the electron transfer in PS I which moves from the primary donor to the final acceptor and therefore away from the semiconductor surface as in the p-GaAs/PS I junction. This novel pathway is driven by an energy gap of −0.9 eV and possibly being mediated through a highly conducting tryptophan pair in the protein and an efficient electronically coupled junction fabricated by covalent binding of PS I to the GaAs surface. The efficient and fast charge transfer may qualify the use of PS I as an optoelectronic component that can be used in integrated circuits such as photoswitches, FET transistors, and photovoltaic cells. We have also demonstrated that TRPL is a useful tool in resolving the physics of molecular interaction between optically active biological proteins and semiconductors.

Supporting Information Available: Detailed calculations and schematic figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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