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Photovoltaic Activity of Photosystem I-Based Self-Assembled Monolayer

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Hybrid protein−metal junctions have potential applications in nanoelectronic devices which can make use of the outstanding catalytic properties of the proteins. Specifically, photoactive proteins are promising materials for optoelectronic applications, such as solar cells and photodetectors.[1] However, very little is known about the electronic coupling between proteins and metal surfaces. Even less is known about the interface between solid surfaces and dry proteins because most proteins are denatured when dried or when they are covalently bound to surfaces. In this work, Kelvin probe force microscopy (KPFM) and surface photovoltage (SPV) spectroscopy techniques are used to study the interaction between a dry oriented monolayer of optically active photosystem I (PS I) proteins and a gold surface.

PS I (Figure 1a) is a transmembrane multisubunit protein−chlorophyll complex that mediates vectorial light-induced electron transfer. Its nanosize dimension, an internal energy yield of approximately 58% (∼23% of solar radiation), and a photovoltage of 1 V with a quantum efficiency approaching 1[2] make the reaction center a promising unit for applications in molecular nanoelectronics. The robust PS I used in these experiments, isolated from the thylakoid membranes of cyanobacteria, is sufficiently stable to be used in hybrid solid-state electronic devices. The structural stability is due to the hydrophobic interaction that integrates 96 chlorophyll, 22 carotenoid pigment molecules and the transmembrane helixes of the core subunits.[3] The electron-transport chain in PS I contains a special pair of chlorophyll *a* (Chl *a*) molecules (P700) that transfer electrons following photoexcitation of a monomeric Chl *a* through two intermediate phylloquinones (PQs) and three [4Fe−4S] iron sulfur (FeS) centers. Recently, we fabricated a self-assembled oriented PS I-based monolayer by formation of a direct sulfide bond between unique cysteine mutants of PS I from cyanobacteria and a metal surface.[4] The dry monolayer generated a photovoltage of 0.45 V when illuminated by monochromatic light at 632 nm.

Figure 1b presents an atomic force microscopy (AFM) image of the PS I monolayer on a gold surface, which clearly shows a dense array of 15- to 21-nm-sized particles, as expected from the size of PS I obtained by crystallography.

A novel KPFM system that uses a 1300 nm wavelength feedback laser which is not absorbed by the PS I molecules (Supporting Information) was used to determine the optical activity of the monolayer. Illumination of the PS I monolayer with 632 nm laser light caused a dramatic reversible increase of 0.452 V in the contact potential difference (CPD) (Figure 1c). The photovoltage in all PS I molecules in the monolayer had the same orientation as was shown earlier.[4] The photovoltage change was caused by the light-induced charge separation that drives electron transfer across the reaction center, which results in the appearance of a negative charge at the reducing end of the protein away from the gold surface. When the light is turned off, charge recombination takes place and the photovoltage nulls. The direct covalent binding resulted in an

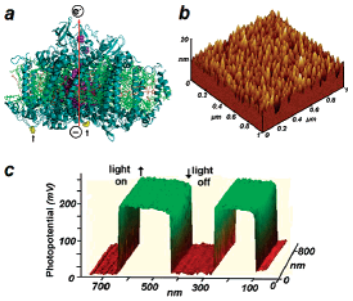

Figure 1. (a) Scheme of the molecular structure of photosynthetic reaction center I (PS I) based upon crystallographic data. PS I is composed of polypeptide chains (cyan) in which chlorophyll (green) and carotenoids (brown) are imbedded. The red arrow schematically depicts the light-induced charge separation across PS I. The chromophores which mediate the electron transfer are represented by the space-fill model (cyano). The PS I covalently binds to the gold surface through Cys mutations along the polypeptide backbone (space-fill model, yellow) which are located on the oxidizing side of the PS I (bottom of the diagram and indicated by black arrows). (b) AFM topography images of oriented PS I monolayer. (c) KPFM images of the PS I monolayer on a gold surface. Excitation by light induced a reversible change of ∼0.45 V in the surface potential.

electronically coupled junction between Au and PS I that caused a loss of about 0.5 V in the photopotential compared to a calculated 1 V because of the solid-state energy difference of ∼0.5 eV between Au and P700 (legend to Figure 2). However, no loss was observed when single PS I was insolated from a gold surface by a mercaptoethanol amine monolayer,[5] yet the monolayer was only partially oriented because of the lack of covalent binding to the Au.

To measure the energy-resolved spectrum of the PS I monolayer, SPV technique was utilized. SPV spectroscopy is a contactless, nondestructive, sensitive technique often used to measure the influence of illumination on the electronic properties of semiconductor and metal−organic surfaces.[6] The SPV measurements were compared to absorption spectra in solution and to the reflectance spectrum of a physisorbed concentrated PS I drop dried on a silicon surface (Figure 2, inset).

SPV spectra of the bound and oriented PS I monolayer on gold shown in Figure 2 (top) indicates that the PS I monolayer retains its fundamental spectral features on the solid surface. Two main photopotential maxima are identified in the SPV spectra, near 420 and 670 nm, corresponding to chlorophyll absorption, as can be seen by comparison to the reflectance and absorption spectra. The similarity between the absorption and SPV spectra is a clear indication that photon absorption by chlorophyll indeed induces charge separation across PS I. This charge separation generates the observed photopotential.

The spectral response of the photovoltage is a direct proof that PS I has not significantly changed its structure or optical activity on the solid surface relative to its native form. However, the SPV spectrum is broader and slightly blue-shifted, by approximately 10−20 nm when compared to the absorption spectra. Such broadening

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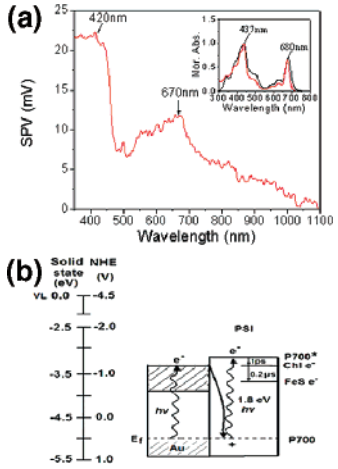

Figure 2. (a) SPV spectra of a PS I monolayer adsorbed to a gold surface and its energy scheme. Inset: Reflectance spectra of a dried concentrated PS I drop on a silicon surface (black curve) and in solution (red curve). Main frame: SPV spectra of PS I monolayer on gold. The SPV spectrum was obtained by subtracting the flat SPV gold, signal which showed no response to light, from the SPV signal of the PS I monolayer on gold. (b) Schematic representation of the gold−PS I junction energy levels diagram. The energies were determined by measurements of CPD compared to a graphite standard. The redox potentials of PS I at pH 7[2] were converted to NHE values by addition of 0.41 V. The scale on the left shows the solid-state energy levels in relation to the NHE redox levels.[7] The solid-state Fermi energy level (E_F) for gold was −5.1 eV,[8] and energy levels between 1.7 and 1.1 eV of the excited electrons are indicated. The energy levels in PS I are −4.58, −2.78, −3.06, and −3.52 eV for the primary electron donor (P700), excited P700*, the primary Chl, and the final FeS electron acceptors, respectively.

can be explained by coupling of PS I to the electronic energy states of the gold, which induces substantial mixing between the molecular and substrate wavefunctions.[9]

The photovoltage detected by the SPV method was smaller than that measured by KPFM. Two factors contribute to this observation. Although PS I forms a fairly dense monolayer, there are still voids and spaces between single excited electrons in each molecule. Thus, the KPFM technique, which probes individual proteins, can detect a higher signal than the SPV technique which averages over surface area detecting a non-continuum dielectric medium. In addition, lower excitation power was used in the SPV measurements as compared to the KPFM method.

Of special interest is the unexpected observed extension of the photovoltage at wavelengths between 730 and 1100 nm, which is beyond the known absorption spectrum of PS I (Figure 2a, inset). It is proposed that photons absorbed between 730 and 1100 nm (1.7−1.1 eV) at the gold−PS I interface excite electrons from the gold (work function of 5.1 V) to higher energy states (by 1.1−1.7 eV). The excited electrons have sufficient energy to reduce the partially oxidized P700 at a solid-state energy of −4.58 eV (Figure 2b), forming a new quasi-equilibrium which generates the observed extended photopotential. These findings are in agreement with recent SPV studies of metal-free tetraphenylporphyrin deposited on gold substrates[10] which identified molecular bonding at the interface as a source for the extended photovoltage spectra. Excitation at the molecular−metal interface states with low-energy photons, although insufficient to excite the molecular electronic states, resulted in the appearance of a photovoltage signal tail extending to low excitation energies. The appearance of this signal was due to electron transfer from the gold to the organic layer. No such effect was reported when PS I was indirectly connected by a tatter extended from the quinone to gold nanoparticles bound to a silane−thiol-modified Si on FET transistor in solution.[11]

Using the Moser and Dutton[12] derivation of the Marcus theory for electron transport, which was used extensively to estimate the rate of electron transfer between components in photosynthetic reaction centers, we estimated that electron transfer between the gold and P700 can proceed at a rate with a lifetime of picoseconds to nanoseconds. The free energy change and the rate of electron transfer support our suggestion that the extended SPV spectrum is due to electronic coupling between P700 and the exited electrons at the gold surface.

In summary, we show that a dry PS I monolayer on a gold surface retains its fundamental optoelectronic properties, as reflected by the similarity between the absorption spectra and the SPV spectral response. Furthermore, adsorption gives rise to new electronic properties which are no longer purely molecular, but a result of the coupled molecular−metal interface. These are new molecule/substrate states yielding energy levels different from those of the individual components. The hybrid system can therefore no longer be considered a sum of its individual components but rather a new entity, resulting from the mixing of the molecular and surface electronic states. Such observations on the coupling between PS I and a gold surface are important when considering device applications. The new monolayer gold properties are expected to increase the spectral range of PS I photon absorption and thus improve the energy-conversion efficiency of PS I-based devices such as photocells and sensitive light detectors.

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Supporting Information Available: Experimental details as cited in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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