Applied Photosynthesis: Photoelectrochemistry of Photosystems

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Photosynthesis is the process by which plants, algae, and cyanobacteria convert our most abundant energy source (solar radiation from the sun) into stored energy in the form of reduced carbon. This process has supported the energy demands of the earth since the beginning of life, and continues to fuel our ever increasing demand. Unfortunately, the release of this stored energy has, in recent years, resulted in numerous problems such as climate change, political unrest, and insufficient supply chains. Thus, a tremendous effort has been put forward in the area of alternative energy research in order to provide new avenues to convert and store energy. The idea behind *applied photosynthesis* is to integrate specific materials derived from photosynthetic organisms into solar energy conversion devices. Photosystem I (PSI) and Photosystem II (PSII) are two protein complexes found in the thylakoid membrane in plants that are responsible for electron excitation in the process of photosynthesis.

PSI is a ~500 kDa membrane protein complex found in most organisms that perform oxygenic photosynthesis. In the process of photosynthesis, PSI operates as a photodiode, photoexciting electrons across the thylakoid membrane in roughly 1 µs. The speed and efficiency of this charge transfer and separation is due to the protein's ability to move the excited electron down an internal electron transfer chain. The energy of each step is slightly lower than the proceeding step, thus thermodynamically favoring a unidirectional electron flow. Once the electron reaches the terminal iron-sulfur complex (FB), it is ushered along to the next step of photosynthesis by the redox protein ferredoxin. At the other side of the protein, the vacant "hole" at the reaction center (P700) is filled with an electron from the copper containing protein known as plastocyanin. PSII performs in a similar manner; however it derives its original electron directly from water. The extraordinary internal quantum efficiency of these photosystems, approaching 100%, have made PSI and PSII unique materials to study in non-biological settings.[1]

Over the past decade, great strides have been made in the use of PSI and PSII for *applied photosynthsis*. Researchers around the globe have moved this research area from an interesting idea to a viable method for producing electricity (photovoltaics)[2-5] and fuels (hydrogen).[6-8]

Our own research group at Vanderbilt University has seen an exponential growth in photocurrent production from biohybrid electrodes based on PSI. Changing the method of protein attachment,[9] electrode geometry,[10] protein film thickness,[11] electrochemical mediator,[12] and electrode materials[13] have all had a pronounced effect on these systems.

In this presentation, we will discuss the relevance of this research in the context of global energy demand, material availability, and future applications. We will describe some of the newer methods and directions that researchers are taking to further improve the photocurrent and photovoltages that these biohybrid systems can produce.

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