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Ultrafast 2D spectroscopy probes charge separation in the plant photosystem

A team of researchers led by IBEC and ICFO has developed and validated a novel photoelectrochemical electron spectroscopy technique to probe charge separation dynamics, a crucial step for photosynthesis, in photosynthetic complexes.

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Photosynthesis is the process by which some organisms (for instance, plants, algae and some bacteria) transform light energy into chemical energy. This process begins with the absorption of light (photons) by certain pigments (mainly chlorophyll) and ends with a flow of electrons that triggers the synthesis of energy carriers.

One intermediate step that has not been directly probed yet, mainly because it occurs at ultrafast timescales, is the so-called **charge separation**. Once the pigment absorbs a photon, an electron is excited to a higher energy level. This extra energy is then transferred to specific locations, called reaction centers, causing an electron of the chlorophyll in those centers to be again excited and transferred to another complex (the acceptor molecule). Consequently, the chlorophyll becomes positively charged, which means that charge separation has occurred. This charge difference is crucial because it sets up a flow of high-energy electrons that will drive the rest of the photosynthetic process.

To decipher photosynthetic complexes and engineer novel photosynthetic strategies, it is thus key to probe the pathways leading to charge separation. This phenomenon has recently been tackled in a joint work between IBEC and ICFO researchers **Dr. Luca Bolzonello** and **ICREA Prof. Niek F. van Hulst**, also in collaboration with the University of Padua and Vrije Universiteit Amsterdam. The team has developed and validated a novel Photoelectrochemical Two-Dimensional Electronic Spectroscopy (PEC2DES) technique, which allows for the direct probing of charge separation dynamics in photosynthetic complexes. Their method was presented in ACS Applied Materials and Interfaces.

ï¿½I think our results are very significant because **we have provided a new way to directly access the biologically relevant charge separation processes, which are crucial for understanding photosynthesis**ï¿½, remarks Dr. Luca Bolzonello, first co-author of the articl
. Unlike traditional optical methods, PEC2DES uniquely combines photoelectrochemic
l detection (PEC) with nonlinear spectroscopy (2DES), allowing for the selective investigati

n of the charge separation event and offering insights into the excitation and charge transf r dynamics within complex photosynthetic systems. More importantly, this technique c n study the ultrafast dynamics of the excitons within the system just by reading out directly t e product of the photosynthesis, that is, the electrical charges that move across the electr n transport chai

Combining PEC and 2DES to obtain PEC2DES

To validate their method, researchers employed photosystem complex I-light harvesting complex I (PSI-LHCI) as model system, where light harvesting by ?antenna chlorophylls' is used to drive charge separation in the reaction center.

They first developed the photoelectrochemical setup (PEC) to measure the current generated by the PSI-LHCI complexes. Then, they integrated this setup with a two-dimensional electronic spectroscopy (2DES) system. **This unprecedented combination of PEC and 2DES gave rise to the PEC2DES technique reported on their study, which for the first time identified the generated charges during charge separation.**

ï¿½The main obstacles we encountered were the need to maintain sample stability over lo g periods of time, which is required by the 2DES measurements, and the difficulty to interpr t the PEC2DES signalï¿½, recalls Bolzonello. ï¿½Even though we discovered that the tec nique is blind to some ultrafast features, we opened the path to solve the issu

Future perspectives: toward artificial photosynthetic systems

The team has just opened the door to tracking the ultrafast dynamics of charge separation processes with the PEC2DES technique. In the near future, they would like to refine their tool by identifying and minimizing the effects of incoherent mixing, an undesired phenomenon that contaminates the object of study, in this case, the charge separation dynamics. They also consider exploring the application of this technique to other photosynthetic complexes or aiming to artificial systems where the effect of incoherent mixing, the main limit of this new technique, is minimized.

According to the researchers, the discovery could be used in biohybrid devices and sensors that rely on the precise control and understanding of electron transfer processes within complex protein assemblies. Bolzonello further guesses that one of the promising applications of PEC2DES could be ï¿½the design and optimization of artificial photosynthet c systems, which in turn could improve solar energy conversion efficiency.ï

Reference:

Manuel Lopez-Ortiz, Luca Bolzonello, Matteo Bruschi, Elisa Fresch, Elisabetta Collini, Chen Hu, Roberta Croce, Niek F. van Hulst, and Pau Gorostiza. ACS Applied Materials & Interfaces 2024 16 (33), 43451-43461. DOI: 10.1021/acsami.4c03652

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