Investigation of Water Splitting Mechanisms in Photosystem II Using Near-IR Resonance Raman Spectroscopy

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Photosynthesis, a process present in algae, green plants, and cyanobacteria, converts sunlight into energy that sustains all living beings on Earth. Photosystem II (PSII) catalyzes the light-driven water oxidation in the process of light to energy conversion. [1]. This reaction is driven by the Mn4Ca complex, which transitions through four stable states (S0 to S4) as described in Kok's cycle, and is embedded in the thylakoid membrane [2]. The exact mechanism of water splitting by the Mn4Ca cluster and the intermediate structural changes of the catalyst during this process are still not fully understood [3]. Previously, some studies using FTIR spectroscopy have attempted to explain this mechanism [4], but Near-IR resonance Raman spectroscopy shows potential for additional approach in understanding of this process. In this study, PS II-enriched thylakoid membranes were prepared from spinach [5] and Near-IR resonance Raman spectra (at 830 nm excitation) were recorded from these freshly prepared PS II samples at room temperature and on cryostage. The addition of hydroxylamine solution which reduces Mn4Ca cluster to Mn2+ ions and results in its destruction resulted in changes of the Raman peaks of PS II sample indicating contribution of Mn4Ca cluster vibrations. Two laser pulses were used to transition PS II from the S1 to S3 state, and the corresponding resonance Raman spectra were recorded at nearly 77K temperature. Thereafter, a 50 mM PPBQ solution in DMSO was added as an artificial electron acceptor before excitation using laser pulses to enhance the conversion of the S3 state. The changes in the Raman peaks of Mn in the MnIV oxidation state were analyzed using resonance Raman signal. Additionally, we studied some manganese model compounds, such as $[Mn_2O_2(tPy)_2(H_2O)_2]^{3+}$, to identify Mn's Raman signal using the same Near-IR resonance Raman spectroscopy and laser..

References;

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