Hierarchical Structural Differences Between Green Algae and Cyanobacteria May Lead to Inefficiencies in H_2 and NADPH Production

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Photosynthetic organisms harness energy from the sun to drive photosynthesis, which converts solar energy to chemical energy, storing it in high-energy bonds. In this highly sustainable reaction, photosystems (PS) II and I utilize energy from photons to efficiently separate electrons from the PSs, driving water oxidation and the formation of NADPH (and ATP). Using the native machinery in photosynthetic organisms in conjunction with synthetic catalysts allows us to produce hydrogen gas, a clean and renewable energy source, with only water and sunlight as the starting reagents.[1] Previous work has shown that platinum nanoparticles (PtNP) as well as molecular catalysts can self-assemble with PSI in spinach and cyanobacteria membranes, which allows for solar overall water splitting to generate hydrogen gas.[2] In cyanobacteria, PSI is an abundant trimer protein, ubiquitously found throughout the thylakoid membrane. However, the morphology of thylakoids differs greatly between prokaryotes and eukaryotes. In green algae and plants, thylakoid membranes have stacked regions that are connected by stroma lamella. PSI is typically found in the stroma lamella while PSII is within the stacked region. Additionally, eukaryotic PSI is a monomer and present in much lower concentrations. In this work, we explore how these morphological differences between the thylakoid membranes and PSI may affect hydrogen production efficiencies as well as higher order complex formation between PSI and ferredoxin and ferredoxin-$NADP^+$ reductase. Utilizing the green algae *Scenedesmus obliquus* and *Chlorella vulgaris*, we isolated PSI and examined H_2 and NADPH formation in comparison to isolated PSI from the cyanobacteria, *Synchococcus leopoliensis*. Understanding the fundamental mechanisms of electron transfer between PSII and PSI as well as between PSI and electron acceptors will inform design strategies for sustainable photosynthetic-inspired systems with efficient solar energy conversion and solar fuel synthesis capabilities.

[1]L. M. Utschig and K. L. Mulfort, "Photosynthetic biohybrid systems for solar fuels catalysis" Chem. *Commun.,* **2024**, 60, 10642. DOI: 10.1039/d4cc00774c

[2]L. M. Utschig, S. R. Soltau, K. L. Mulfort, J. Niklas, O. G. Poluektov, "Z-scheme solar water splitting via self-assembly of photosystem I-catalyst hybrids in thylakoid membranes", *Chem. Sci.*, **2018**, 9, 8504. DOI: 10.1039/c8sc02841a