

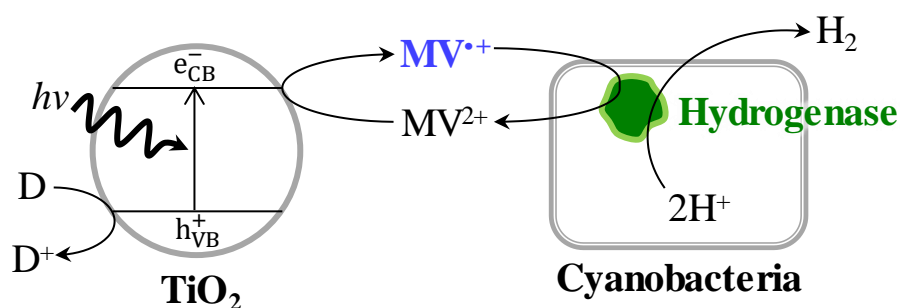
## Cyanobacterial hydrogenase in photobiocatalytic H<sub>2</sub> production

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Solar to H<sub>2</sub> energy conversion is one of the most promising approaches of the future to replace finite fossil fuels, owing to its carbon-free, renewable and environment-friendly system. According to the objectives and research effort of Project 2-1 of our division during 2014-2020, we have been focusing on the optimization of photocatalysts and the application of hydrogenase for H<sub>2</sub> production. Photobiocatalysis has been attractive due to its flexibility, low energy cost, and eco-friendly characteristics. This work aims to discover and apply cyanobacteria and photocatalyst for photobiocatalytic H<sub>2</sub> production. *Anabaena variabilis*, a filamentous cyanobacteria, was cultivated in nitrogen-free Allen & Arnon medium to stimulate the differentiation of heterocyst. A novel application of TiO<sub>2</sub> coupled to the extracted protein of cyanobacterial cells significantly generated H<sub>2</sub> compared to TiO<sub>2</sub> alone. Inductively coupled plasma (ICP) technique reveals the existence of both NiFe-hydrogenase and FeMo-nitrogenase from the amounts of nickel (Ni) and molybdenum (Mo) atoms at their active site, respectively. Both biocatalytic enzymes show a crucial role for H<sub>2</sub> production. In addition, it was found that cyanobacteria can generate ammonia from N<sub>2</sub> fixation in air through a function of nitrogenase enzyme. The achievement of this study is to provide an alternative technique to overcome a major obstacle of O<sub>2</sub> sensitivity that considerably necessary for low-cost application of industrial-scale H<sub>2</sub> production from renewable resource without CO<sub>2</sub> emission.



**Scheme 1** Photobiocatalytic H<sub>2</sub> evolution from the combination of TiO<sub>2</sub> and hydrogenase-expressing cyanobacteria. D = an electron mediator, MV = methyl viologen.