Photobiocatalytic system of GaN:ZnO and hydrogenase-producing *E. coli*

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Solar-to-chemical energy conversion is one of the ultimate goals for clean technology economically in the future. Artificial photosynthesis inspired by natural photosynthetic pathway through coupling photocatalyst and microbial biocatalyst possessing metabolic versatility has become very attractive for a wide range of chemical fuel production. Hydrogen with high energy capacity and without carbon dioxide emission is anticipated to be responsible for 90% of global energy source in 2080. According to the objectives and research effort of our division during 2014-2020, we have been focusing on the optimization of photocatalytic activity and the application of hydrogenase to improve the efficiency and productivity of hydrogen conversion. This study aims to combine GaN:ZnO and hydrogenase-producing *E. coli* as a new artificial photosynthetic system for solar energy-to-hydrogen conversion. GaN:ZnO is a heterogenous inorganic semiconductor with a band gab of <3.0 eV that can harvest photon up to ca. 500 nm. While genetically-engineered *E. coli* carrying 4 hydrogenase genes (HydE, HydA, HydF and HydG) from *Clostridium acetobutylicum* is served as a living biocatalyst. In the light-driven reaction of hybrid system, photocatalytic methylviologen (MV) reduction was applied in various conditions. Reduction rate was influenced by redox potential of electron donor agents in order of triethanolamine (TEOA) > Tris(hydroxymethyl)aminomethane > trimethylamine (TEA). In addition, the rate of MV reduction was significantly accelerated in alkaline condition. However, the efficiency of hybrid system reached the maximum capacity at neutral pH 7 and 8 with hydrogen formation rate of ~160 μmol/h, indicating that biocompatible circumstance is considerable for physiological function of hydrogenase inside bacterial cells. As a visible-light photocatalyst, GaN:ZnO showed the possibility to be performed under sunlight with apparent quantum yield (AQY) of 1.5 % irradiated by light source through a 420-nm bandpass filter. Our study reveals the promising alternatives of GaN:ZnO and hydrogenase-producing *E. coli* as a novel hybrid approach for non-polluting hydrogen production under solar radiation.

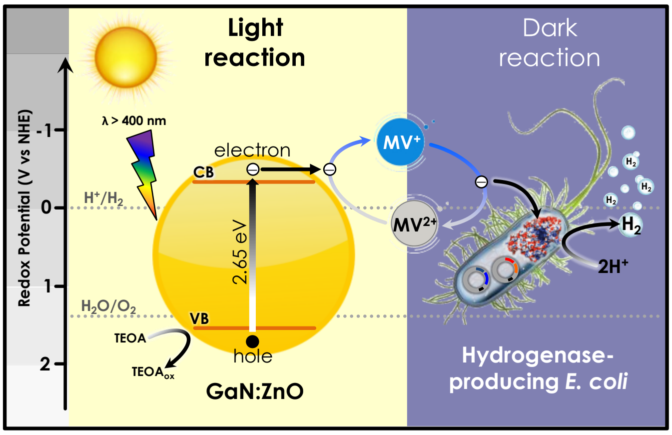

Figure 1 Hybrid system of GaN:ZnO and hydrogenase-producing *E. coli* for hydrogen production