The light-to-chemical energy conversion for hydrogen production using biologically precipitated metal sulfide semiconductor

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Research objective

The use of solar energy has attracted considerable attention for the realization of a sustainable energy society. Solar energy must be stored, transported, and utilized in the form of compounds. Hydrogen as a promising energy storage material, has been the focus of various approaches aimed at achieving efficient hydrogen production using light. This study focuses on constructing a biohybrid system, combining an inorganic semiconductor photocatalyst with an enzyme, to develop a new catalytic system that integrates highly stable, inexpensive, and efficient photochemical energy conversion using inorganic materials with highly efficient material transformation using biocatalysts.

This study builds upon a previously reported biohybrid that combines cadmium sulfide (CdS) formation via microbes with genetically enhanced hydrogen production in *Escherichia coli*[1]. The primary aim of this study to improve the light-hydrogen production capacity of the biohybrid entire system by genetic engineering of the formation of CdS in *E. coli*: enhancement of sulfide synthesis by cysteine desulfhydrolase (DSH), which enhances CdS formation and the light energy conversion capacity (Figure 1).

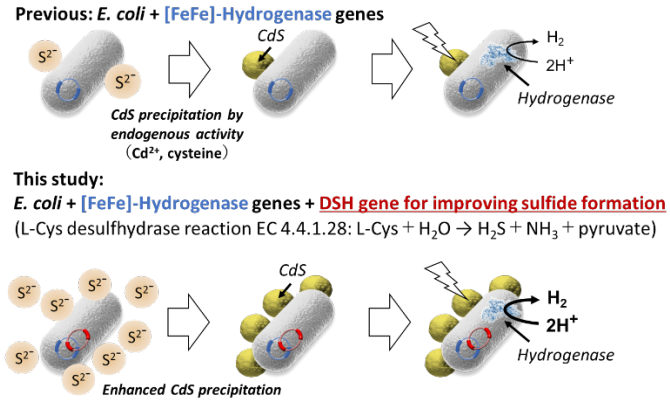

Figure 1 Overview of light driven hydrogen production by the biohybrid

Methods

E. coli BL21 (DE3) was used as the host for protein production. The production of [FeFe]-hydrogenase was carried out using *E. coli* transformed with pEHydEFG-A[2], following a

method reported previously[1]. The pBAD-DSH plasmid was constructed by connecting the DSH gene from *Treponema denticola* into pBAD33 and was used to enhance sulfide synthesis capacity in *E. coli*. *E. coli* BL21(DE3)/pEHydEFG-A, *E. coli* BL21(DE3)/pEHydEFG-A+pBAD-DSH, and *E. coli* BL21(DE3)/pEHydEFG-A+pBAD33 were called *E. coli* Hyd+, *E. coli* Hyd+/DSH+, and *E. coli* Hyd+/DSH−, respectively. The DSH activity was assessed by measuring sulfide production from cysteine using the methylene blue method. CdS formation in *E. coli* was performed using a method reported previously[1]. An integrating sphere was used to measure the absorbance of the *E. coli* suspensions. CdS formed by *E. coli* was isolated and purified to form a CdS film on an ITO glass electrode, which was used as a photoelectrode to measure the photocurrent in 100 mM BisTris-HCl (pH 5) by applying 0 V (vs. Ag/AgCl) and exposing to a 405 nm LED light. The localization of CdS was evaluated by transmission electron microscopy. Light-driven hydrogen production was performed using an AM1.5 G sunlight simulator according to a method described previously[1].

Results

Sulfide production was determined by adding 1 mM cysteine to cell suspensions of *E. coli* Hyd+/DSH+ and *E. coli* Hyd+ (Figure 2a), showing enhanced sulfide formation by the introduction of the DSH gene. The changes in CdS formation by the introduction of the DSH gene were confirmed; *E. coli* subjected to CdS formation were collected at each time point, and the absorbance of the cell suspension was monitored (Figure 2b). In *E. coli* Hyd+/DSH+, CdS formation started in the UV region at 1 h, and by 3 h, the absorbance appeared in the visible region from 400 to500 nm absorption. *E. coli* Hyd+ showed no significant absorption in the UV region, and absorption at 450 nm appeared after 10 h. Previously, CdS formation required 20 h[1], but the introduction of the DSH gene shortened the time required for CdS formation. The photocurrent of the CdS formed by *E. coli* also enhanced the light-to-chemical conversion of CdS by introducing the DSH gene (Figure 2c). TEM observations showed that CdS formation initially occurred intracellularly and that CdS accumulated in the periplasm (Figure 2d). Finally, the enhancement of light-driven hydrogen production by the introduction of the DSH gene was confirmed. Figure 2e shows the absorption of 10-h CdS formation in *E. coli*. Hydrogen production under AM1.5G light irradiation by the sunlight simulator (Figure 2f) was improved by the DSH gene, reflecting the fact that *E. coli* Hyd+/DSH+ showed visible light absorption. *E. coli* Hyd+/DSH+ showed improved light-driven hydrogen production capacity under visible light compared to *E. coli* Hyd+ used in a previous study[1].

Conclusion

Enhancing the sulfide synthesis ability of *E. coli* by introducing the DSH gene shortened the formation time of the CdS nanoparticles and improved the light-to-chemical energy

conversion capacity per weight of CdS. This enhancement of light-to-chemical energy conversion successfully improved the overall light-driven hydrogen production by the biohybrid[3].

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References

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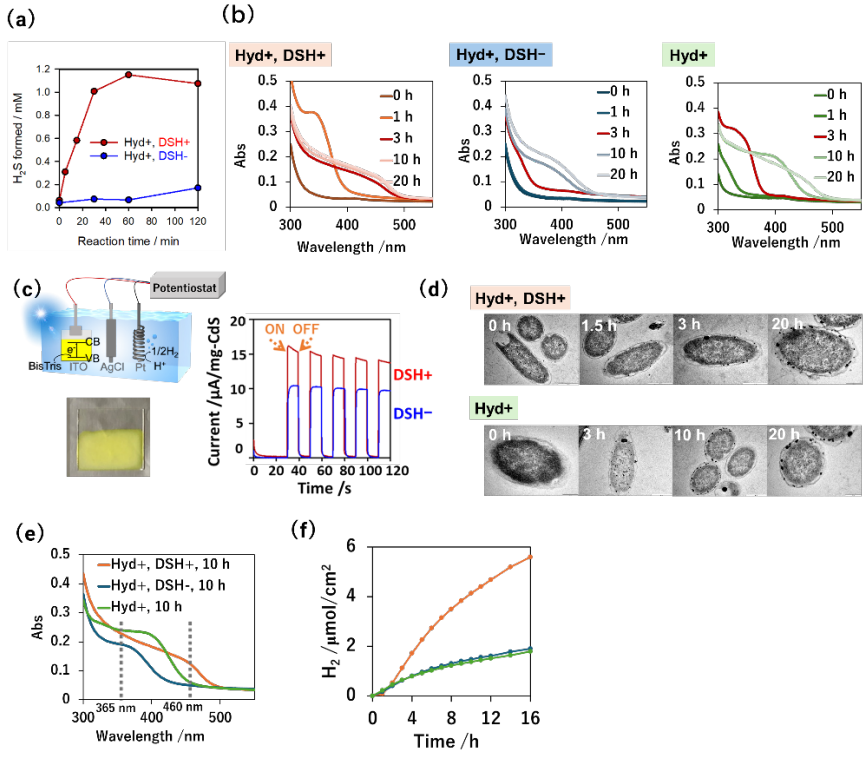

Figure 2 Enhancement of the light-to-chemical energy conversion capacity of biohybrid by DSH gene. (a) DSH activity, (b) absorbance of *E. coli* strains after CdS formation, (c) photocurrent measurement, (d) TEM observation, (e) absorption at 10-h CdS formation, (f) light-driven hydrogen production under AM 1.5G irradiation for the biohybrid.