



Methanol production from CO₂ with the hybrid system of biocatalyst and organo-photocatalyst

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ABSTRACT

Photochemical and enzymatic production of methanol from CO₂ was investigated with the system formate (FDH), aldehyde (AldDH) and alcohol (ADH) dehydrogenases, and methylviologen (MV²⁺) photoreduction by the visible light photosensitization of organo-photocatalyst, water-soluble porphyrin, tetraphenylporphyrin tetrasulfonate (H₂TPPS) in the presence of triethanolamine (TEOA) as an electron donating reagent. To improve the methanol production from CO₂, the kinetic parameters for methanol production with ADH and dithionite-reduced MV²⁺ were clarified. When the sample solution consisting of H₂TPPS (100 μM), MV²⁺ (2.0 mM), TEOA (0.3 M), FDH (2.0 μM), AldDH (2.0 μM) and ADH (2.0 μM) in CO₂ saturated 50 mM sodium pyrophosphate buffer was irradiated, continuous methanol production from CO₂ was observed and methanol concentration produced was estimated to be 6.8 μM after 100 min irradiation.

1. Introduction

Photoredox system consisting of an electron donor, a photosensitizer, an electron carrier and catalyst is widely used for the photochemical conversion system such as hydrogen production, CO₂ reduction to organic molecules and so on [1–5]. This system is a mimicking and simplification of the photosynthesis reaction, thus, is used as a model of artificial photosynthesis for solar fuel production. By using reduced form of electron carrier as a second substrate for the catalyst in this system, hydrogen production based on the proton reduction and CO₂ reduction systems are developed. For photoinduced hydrogen production systems, platinum nano-particle and biocatalyst, hydrogenase have been widely used as catalysts [6–10]. The photochemical and enzymatic conversion of organic compounds has also been developed using this system in the presence of various redox biocatalysts [11–23]. Redox biocatalysts, dehydrogenases such as lactate (LDH), formate (FDH), aldehyde (AldDH) and alcohol dehydrogenase (ADH) are useful catalysts for the conversion of valuable organic compounds such as lactic acid, formic acid, methanol *etc.* For example, we reported the pyruvic acid conversion to lactic acid production with LDH and the reduced form of methylviologen (MV²⁺) produced by the visible light photosensitization of water soluble zinc tetrakis(4-methylpyridyl) porphyrin (ZnTMPyP) [22]. The advantage of

the combination of photoredox system and biocatalyst is that only the desired product is obtained with the visible-light irradiation

In the photoredox system, the effective organo-photocatalyst is an essential component. Organo-photocatalyst, porphyrins are widely used as effective visible-light sensitizers [24,25]. As water soluble porphyrins have a strong absorption bands in the visible light region (380 – 600 nm), these porphyrins are more widely used as an effective photosensitizer [26–29].

Methanol is paid much attention to the lower carbon fuel. Thus, we devoted to the methanol production from CO₂ and water with coupling the photoredox system, some biocatalyst and inorganic catalyst as shown in Fig. 1. One of the important steps is the photochemical methanol production from CO₂ using combination of photoredox and biocatalyst system. By using natural co-enzyme nicotinamide adenine dinucleotide (NAD⁺) or reduced form (NADH), FDH catalyses both the reduction of CO₂ to formic acid and the oxidation of formic acid to CO₂, AldDH catalyses both the reduction of formic acid to formaldehyde and the oxidation of formaldehyde to formic acid, and ADH also catalyses both the reduction of formaldehyde to methanol and the oxidation of methanol to formaldehyde as shown in Fig. 2. Thus, it is necessary to suppress the oxidation processes with FDH, AldDH and ADH for the conversion of CO₂ to methanol. Moreover, the NAD dimer is formed between the one-electron reduced form of NAD⁺s with organo-

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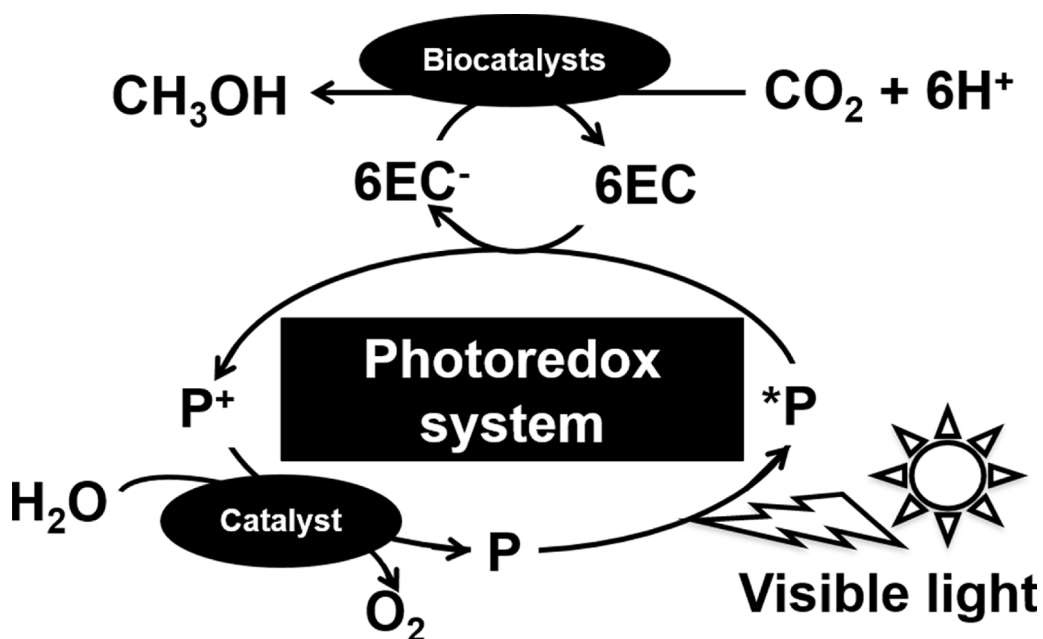


Fig. 1. Concept of visible-light induced methanol production from CO_2 and water with the coupling system of photoredox, catalyst and biocatalyst. P: Photosensitizer based on organo-dye molecule, EC: electron carrier molecule.

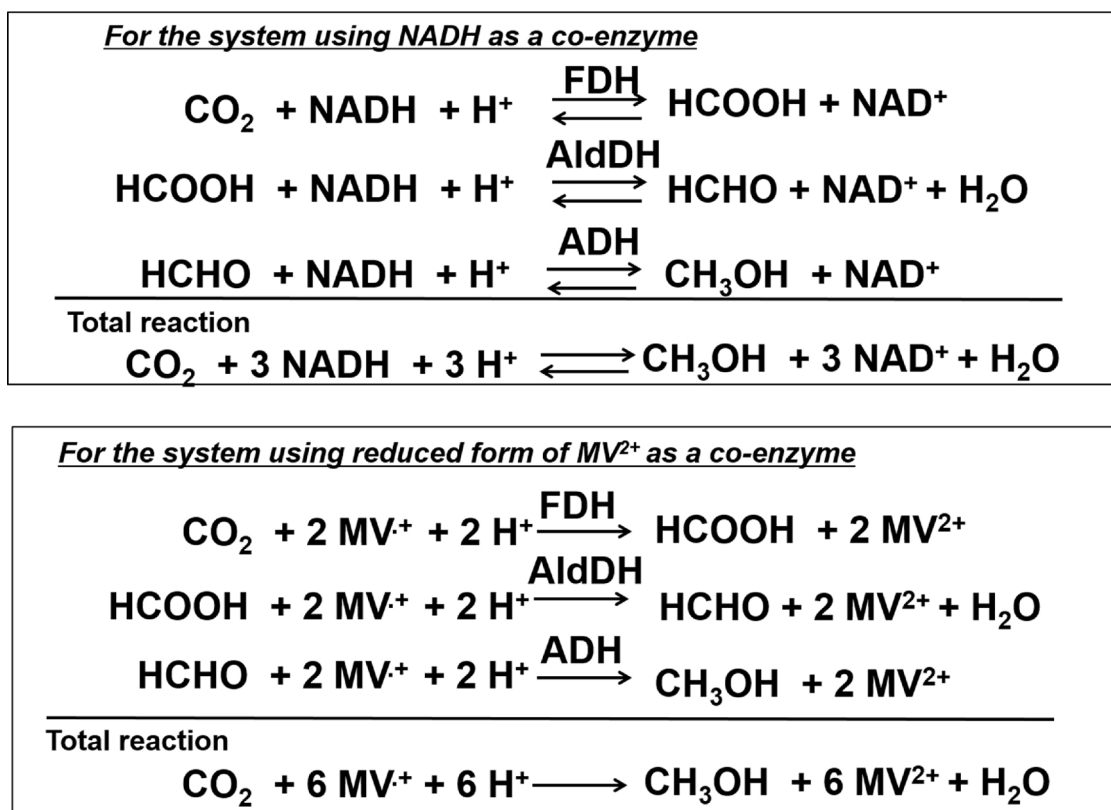


Fig. 2. Scheme for the methanol production from CO_2 with FDH, AldDH and ADH using natural co-enzyme NAD^+/NADH and artificial co-enzyme $\text{MV}^{2+}/\text{MV}^+$.

photocatalyst [30]. Even if the NAD^+ reduction to NADH with photoredox system could be achieved, NAD^+ is a very expensive biological reagent and, it is necessary to improve its usage and turnover of the redox coupling of NAD^+/NADH . As long as the redox coupling of NAD^+/NADH is used, the affinity between NAD^+ or NADH and biocatalyst does not change, thus, biocatalyst activity can not be controlled in the photoredox system. As the produced NADH acts as a sacrificial reagent and is consumed, moreover, the redox coupling of NAD^+/NADH is not suitable to use for the photoredox system. As the NAD

dimer is an inactive co-enzyme for NAD^+ -dependent dehydrogenases, it is difficult to achieve the system via the combination of NAD^+ photo-reduction and NAD^+ -dependent dehydrogenase. In contrast, we found that the reduced form of MV^{2+} only acts as a co-enzyme for FDH, ADH and AldDH, and oxidized form of MV^{2+} is not recognized for a co-enzyme of FDH, ADH and AldDH [31–35]. Thus, the oxidation processes with FDH, AldDH and ADH suppressed using oxidized form of MV^{2+} as an electron carrier molecule as shown in Fig. 2. As MV^{2+} easily is reduced using photoredox system with organo-photocatalyst,

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