Visible light-driven building C-C bonds from CO_2 as a feedstock with photosensitizer-biocatalyst hybrid system

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Abstract: CO_2 utilization has received much attention. In particular, biocatalyst, malic enzyme (ME) catalyzes the reaction of malate to pyruvate and CO_2, and the reverse reaction. Thus, ME is an attractive biocatalyst for building C-C bonds from CO_2. Studies of the visible light-driven malate production from pyruvate and CO_2 using an electron donor, a photosensitizer, an electron mediator, ferredoxin-$NADP^+$ reductase, $NADP^+$, and ME have been reported. However, these systems are complicated. In this study, the visible light-driven building C-C bond from pyruvate and CO_2 with ME using the reduction of 1,1'-diphenyl-4,4'-bipyridinium salt as an electron mediator with water-soluble porphyrin was developed.

Keywords: Biocatalyst, Building C-C bonds, CO_2 utilization, Photoredox system.

1. Introduction

Recently, solar fuels such as hydrogen gas from water splitting, and low-carbon fuels such as CO formic acid, and methanol from CO_2 reduction have received considerable attention. Typical photoredox systems activated by visible light irradiation, consisting of an electron donor (D), a photosensitizer (P), an electron carrier (C) and catalyst have been reported. By using the reduced form of an electron carrier (C^-) as a coenzyme for the biocatalyst, hydrogen production and CO_2 conversion by solar fuel production systems were developed. For example, a visible-light driven CO_2 reduction system that combines the photoreduction of an electron carrier through the photosensitization of water-soluble photosensitizer and the reduction of CO_2 using formate dehydrogenase (FDH) were established. In this system, the carbon number of product (C1 product) is not extended due to CO_2 reduction. Next, the target of the photoredox system is the building C-C bonds from CO_2 as a feedstock. Malic enzyme (ME) catalyzes the reaction of malic acid to pyruvic acid and CO_2 with the co-enzyme $NADP^+$, and catalyzes the reverse reaction of pyruvic acid and CO_2 to malic acid with co-enzyme NADPH. Thus, ME is also an attractive biocatalyst for the building C-C bonds from CO_2. Several studies on the visible-light driven malic acid from pyruvic acid and CO_2 with the system consisting of an electron donor (D), a photosensitizer (P), an electron mediator (C), ferredoxin-$NADP^+$ reductase (FNR), $NADP^+$, and ME as shown in Fig. 1 (system 1) have been reported. [1)] However, as this system is very complicated, it is necessary to simplify it by using an electron mediator (DPV^{2+}) instead of $NADP^+$ reduction, as shown in Fig. 1 (system 2). In this study, the visible-light driven building C-C bonds from pyruvic acid and CO_2 with ME using the photoreduction of DPV^{2+} with water soluble tetraphenylporphyrin tetrasulfonate (H_2TPPS) in the presence of TEOA as an electron donor was developed, as shown in Fig. 1 (system 2; D: TEOA, P: H_2TPPS, DPV^{2+}:1,1'-diphenyl-4,4'-bipyridinium salt).

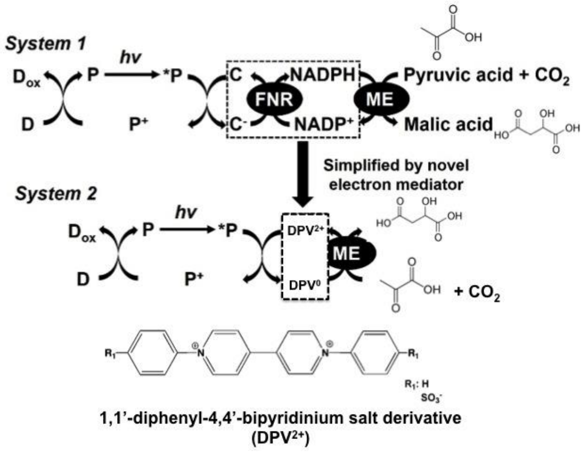

Figure 1. Visible-light driven malic acid from pyruvic acid and CO_2 with the system consisting of an electron donor (D), (D), a photosensitizer (P), an electron mediator (C), ferredoxin-$NADP^+$ reductase (FNR), $NADP^+$ and ME (system 1) and the simplified system using a novel electron mediator (DPV^{2+}) (system 2).

2. Experimental

1,1’-Diphenyl-4,4’-bipyridinium salt derivative, 1,1’-bis(*p*-sulfonylphenyl-4,4’-bipyridinium dichloride (PSV^{2+}) was synthesized according to a previously-reported method with some modifications. The first and second reduction potentials for 1,1‘-bis(*p*-sulfonylpheny)-4,4‘-bipyridinium dichloride (PSV^{2+}) were determined by cyclic voltammetry using an Ag/AgCl electrode as the reference in pH 7.4 sodium pyrophosphate buffer containing 0.1 mM KCl. UV-vis absorption spectra of oxidized, one-electron and two-electron reduced form of PSV^{2+} were measured. The sample solution containing H_2TPPS (40 μM), PSV^{2+} (0.4 mM), TEOA (0.2 M), pyruvic acid (6.0 mM) and ME (4.0 units) in 3.0 ml of CO2 saturated 5.0 mM Bis-tris buffer (pH 7.4) was irradiated with a 250 W halogen at 30 ˚C. The amount of oxaloacetic acid as an intermediate or malic acid as a product was detected by an ionic chromatograph system (Dionex IC2000).

3. Results and discussion

The first and second reduction potentials for PSV^{2+} (*vs* Ag/AgCl) were estimated to be −0.34 and −0.64 V, respectively.

The absorption maxima of oxidized, one-electron and two-electron reduced form of PSV^{2+} were around 400, 500 and 700 nm, respectively.

When the reaction mixture containing H_2TPPS (40 μM), PSV^{2+} (0.4 mM), and TEOA (0.2 M) in 3.0 ml of 5.0 mM Bis-Tris buffer (pH 7.4) was irradiated with visible light, the absorbance attributed to the absorption band for two-electron reduced form of PSV^{2+} at 688 nm increased with irradiation time. In this system, the fluorescence of H_2TPPS was not quenched by PSV^{2+}, and thus, the photoinduced electron transfer from the photoexcited triplet state of H_2TPPS ($^3H_2$TPPS*) to PSV^{2+} proceeded. The oxidation potential for TEOA was reported to be 0.93 V (vs. Ag/AgCl). The redox potentials of the exited triplet state of H_2TPPS, *E*($H_2TPPS^+/^3H_2TPPS^*$) and *E* ($^3H_2TPPS^*/H_2TPPS$) were estimated to be −0.70 and 0.40 V, respectively. The one- and two-electron reduced form of PSV^{2+} were produced with the photosensitization of H_2TPPS.

When a sample solution containing TEOA (0.2 M), H_2TPPS (40 μM), PSV^{2+} (0.4 mM), pyruvic acid (6.0 mM) and ME (4.0 units) in CO_2 saturated Bis-Tris buffer (pH 8.0) was irradiated, oxaloacetic acid (main product) was produced. After 2 h irradiation, 60 μM oxaloacetic acid was produced as shown in Figure 2. However, no malic acid production was observed with the visible light irradiation. Thus, the visible-light driven photoredox system for building C-C bonds from CO_2 with ME using PSV^{2+} as an electron mediator. We are currently studying the mechanisms underlying oxaloacetic acid production from CO_2 and pyruvic acid using the reduced form of PSV^{2+} produced in the photoredox system.

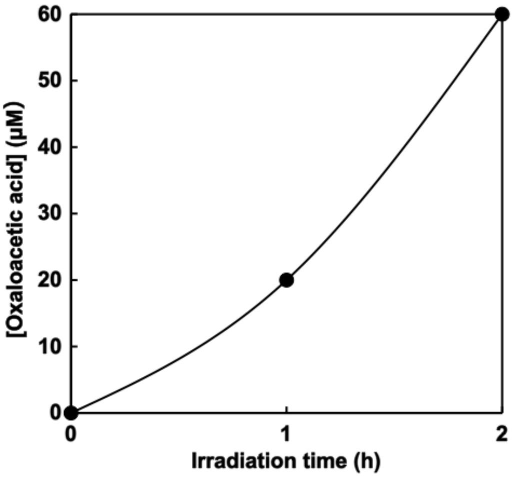

Figure 2. Time dependence of oxaloacetic acid (circle) production with the system containing TEOA, H_2TPPS, PSV^{2+}, ME and pyruvic acid in the CO_2 saturated Bis-Tris buffer under the steady state irradiation.

4. Conclusions

In this study, the visible-light driven building C-C bonds from pyruvic acid and CO_2 with ME using the photoreduction of PSV^{2+} with H_2TPPS in the presence of TEOA was developed for the first time. Thus, we discovered the reduced form of PSV^{2+} the ME activity for building C-C bonds from pyruvic acid and CO_2, and presented a novel approach of building C-C bonds from CO_2 as a feedstock with the biocatalyst.

References

1. Y. Amao, M. Ishikawa, Catal. Commun, 8(2007),523.