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Bacteria-Like Fixation of Carbon Dioxide under UV-Light Irradiation with Defect-Free ZnS Quantum Crystallites

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Photoreduction of CO_2 to formic acid and a small quantity of CO can be achieved effectively in water by using defect-free ZnS quantum crystallites and their aggregates as catalysts and S^{2-} and $H_2PO_2^-$ ions as sacrificial electron donors under >290-nm irradiation.

The reduction of CO_2 to organic materials using abundant natural energy (e.g., solar light) with abundant but unused resources has attracted much interest as artificial photofixation of CO_2[1] to cope with the greenhouse effect.[2] In particular, photoreduction of CO_2 with sulfur compounds like S^{2-} ion is noteworthy from the viewpoint of mimicking bacteria-like carbon assimilation.

In our preceding paper[3] it was reported that defect-free ZnS quantum crystallites and their aggregates catalyze quantitative photoredox reactions of aqueous mixture of 2-butanone, Na_2S, and Na_2SO_3 under >313-nm light irradiation, converting 2-butanone to 2-propanol without much H_2, while S^{2-} and SO_3^{2-} ions used as electron donors are quantitatively photooxidized to $S_2O_3^{2-}$ ion. This paper deals with the effective photoreduction of CO_2 to formic acid (the apparent quantum yield ($\Phi_{1/2HCOOH}$) was 0.23 at 313 nm) and CO which is catalyzed by defect-free quantum ZnS crystallites under comparable conditions.

As reported in a previous paper,[3] the aqueous suspensions of defect-free ZnS quantum crystallites (ZnS-0) were prepared from aqueous solutions of $ZnSO_4$ and Na_2S under argon atmosphere, cooling with an ice bath, and stirring with magnetic stirrer in a Pyrex tube (8 mm in diameter). To 0.5 mL (L=dm^3) of ZnS suspension (ca. 25 μmol) in the tube was added 0.5 mL of a mixture of Na_2S (e.g., 0.24 M (M=mol dm^{-3})) and Na_2SO_3 (e.g., 0.35 M) or NaH_2PO_2 (e.g., 0.35 M) and CO_2 was absorbed into the reaction mixture. The resulting solution was almost neutral (ca. pH 7), which implies that S^{2-} ion should be converted into SH^-.

Figure 1 shows the sequence of photoreduction of carbon dioxide occurring in the presence of both S^{2-} and $H_2PO_2^-$ ions, or both S^{2-} and SO_3^{2-} ions upon >290-nm irradiation. Thiosulfate ion ($S_2O_3^{2-}$) was detected as an oxidation product by ion chromatography.[3] In the former case, formic acid was formed efficiently and competitively with H_2 evolution. After 3 h irradiation, the formation of formic acid has a tendency to decrease, which was explained as due to the consumption of the once-formed formic acid by photooxidation on the irradiated ZnS particles. It is quite unexpected that the dramatic synergistic effect of S^{2-} and SO_3^{2-} was not observed in the photoreduction of CO_2. H_2 was main

reduction product and formic acid was formed in poor yield. A small amount of CO was also formed in both cases. However, formaldehyde, methanol and methane were not detected in this photoreduction.[4)]

The photocatalytic activity of some other ZnS was investigated using both S^{2-} and $H_2PO_2^-$ ions as electron donors. The freshly prepared ZnS-0 suspensions was found most efficient but the powdered one ($ZnS\text{-}100^P$) after heat-treatment (100 ℃, 10 min)[3)] and commercially available ZnS were almost inactive for the reduction of CO_2. These facts suggest that defect-free states of the quantized ZnS should be a requisite for the effective photoreduction of CO_2.

As a source of CO_2, $NaHCO_3$ was not reducible in this system. When CO_2 was introduced to the reaction mixture containing $NaHCO_3$ and the pH of the solution became ca. 9, however, formic acid was formed in a fair yield. As electron donors, tetrahydrofuran and triethylamine were not effective for the present photoreduction of CO_2, although they work as electron donors only for the photoreduction of water to H_2. The similar photoreduction of CO_2 was first reported by Henglein and his group using 2-propanol as sacrificial electron donor under slightly acidic conditions.[5)] However, the reproducibility of the photoreduction seemed to be invariably poor, and one was forced to fail in the photo-production of formic acid.

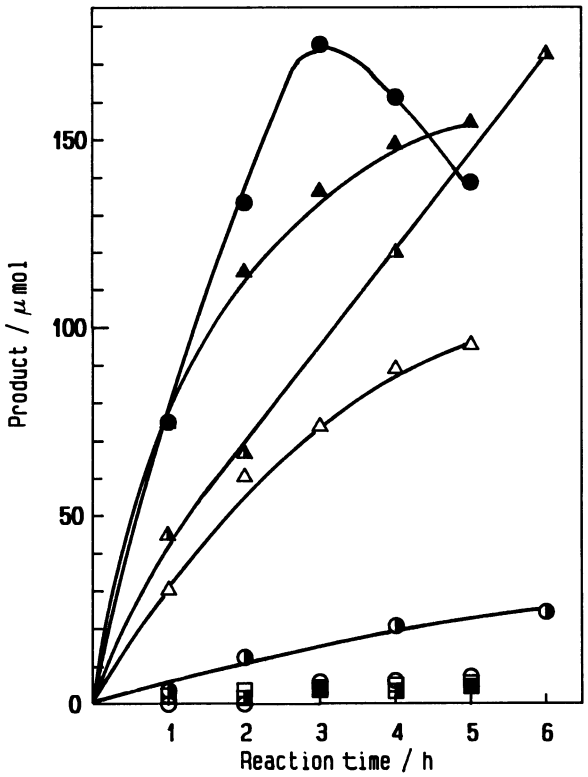

Fig. 1. UV-light-induced bacteria-like fixation of CO_2 in water: using ZnS-0 suspension in the presence of both S^{2-} (0.24 M) and $H_2PO_2^-$ (0.35 M), (●) HCOOH, (■) CO, (▲) H_2; using ZnS-0 suspension in the presence of both S^{2-} (0.24 M) and SO_3^{2-} (0.35 M), (◑) HCOOH, (◨) CO, (◭) H_2; using $ZnS\text{-}100^P$ in the presence of both S^{2-} (0.24 M) and $H_2PO_2^-$ (0.35 M), (○) HCOOH, (□) CO, (△) H_2.

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