

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

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Photoreduction of CO<sub>2</sub> 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<sup>2-</sup> and H<sub>2</sub>PO<sub>2</sub><sup>-</sup> ions as sacrificial electron donors under >290-nm irradiation.

The reduction of CO<sub>2</sub> to organic materials using abundant natural energy (e.g., solar light) with abundant but unused resources has attracted much interest as artificial photo-fixation of CO<sub>2</sub><sup>1)</sup> to cope with the greenhouse effect.<sup>2)</sup> In particular, photoreduction of CO<sub>2</sub> with sulfur compounds like S<sup>2-</sup> ion is noteworthy from the viewpoint of mimicking bacteria-like carbon assimilation.

In our preceding paper<sup>3)</sup> it was reported that defect-free ZnS quantum crystallites and their aggregates catalyze quantitative photoredox reactions of aqueous mixture of 2-butanone, Na<sub>2</sub>S, and Na<sub>2</sub>SO<sub>3</sub> under >313-nm light irradiation, converting 2-butanone to 2-propanol without much H<sub>2</sub>, while S<sup>2-</sup> and SO<sub>3</sub><sup>2-</sup> ions used as electron donors are quantitatively photooxidized to S<sub>2</sub>O<sub>3</sub><sup>2-</sup> ion. This paper deals with the effective photoreduction of CO<sub>2</sub> to formic acid (the apparent quantum yield ( $\Phi_{1/2\text{HCOOH}}$ ) 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,<sup>3)</sup> the aqueous suspensions of defect-free ZnS quantum crystallites (ZnS-0) were prepared from aqueous solutions of ZnSO<sub>4</sub> and Na<sub>2</sub>S 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<sup>3</sup>) of ZnS suspension (ca. 25 μmol) in the tube was added 0.5 mL of a mixture of Na<sub>2</sub>S (e.g., 0.24 M (M=mol dm<sup>-3</sup>)) and Na<sub>2</sub>SO<sub>3</sub> (e.g., 0.35 M) or NaH<sub>2</sub>PO<sub>2</sub> (e.g., 0.35 M) and CO<sub>2</sub> was absorbed into the reaction mixture. The resulting solution was almost neutral (ca. pH 7), which implies that S<sup>2-</sup> ion should be converted into SH<sup>-</sup>.

Figure 1 shows the sequence of photoreduction of carbon dioxide occurring in the presence of both S<sup>2-</sup> and H<sub>2</sub>PO<sub>2</sub><sup>-</sup> ions, or both S<sup>2-</sup> and SO<sub>3</sub><sup>2-</sup> ions upon >290-nm irradiation. Thiosulfate ion (S<sub>2</sub>O<sub>3</sub><sup>2-</sup>) was detected as an oxidation product by ion chromatography.<sup>3)</sup> In the former case, formic acid was formed efficiently and competitively with H<sub>2</sub> 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<sup>2-</sup> and SO<sub>3</sub><sup>2-</sup> was not observed in the photoreduction of CO<sub>2</sub>. H<sub>2</sub> 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.<sup>4)</sup>

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-100P) after heat-treatment (100 °C, 10 min)<sup>3)</sup> 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.<sup>5)</sup> However, the reproducibility of the photoreduction seemed to be invariably poor, and one was forced to fail in the photo-production of formic acid.

#### References

- 1) I. Taniguchi, "Modern Aspects of Electrochemistry, No. 20," ed by J. O'M. Bockris, R. E. White, and B. E. Conway, Plenum Publishing Corporation, New York (1989), p. 327; K. Tanaka, R. Wakita, and T. Tanaka, *J. Am. Chem. Soc.*, **111**, 2428 (1989) and references cited therein.
- 2) B. Hileman, *Chem. Eng. News*, March 13, 25 (1989).
- 3) S. Yanagida, M. Yoshiya, T. Shiragami, and C. Pac, *J. Phys. Chem.*, **94**, in press.
- 4) T. Inoue, A. Fujishima, S. Konishi, and K. Honda, *Nature*, **277**, 637 (1979); B. Aurian-Blajeni, M. Halmann, and J. Manassen, *Solar Energy*, **25**, 165 (1980).
- 5) A. Henglein, M. Gutierrez, and Ch. H. Fischer, *Ber. Bunsenges. Phys. Chem.*, **88**, 170 (1984).

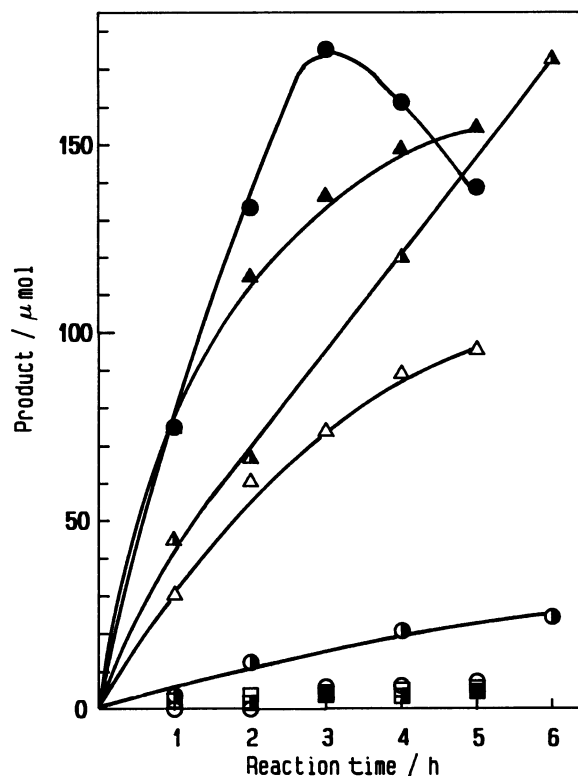


Fig. 1. UV-light-induced bacteria-like fixation of  $CO_2$  in water: using ZnS-0 suspension in the presence of both  $S^{2-}$  (0.24 M) and  $H_2PO_2^-$  (0.35 M), (●) HCOOH, (■) CO, (▲)  $H_2$ ; using ZnS-0 suspension in the presence of both  $S^{2-}$  (0.24 M) and  $SO_3^{2-}$  (0.35 M), (○) HCOOH,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