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Visible-Light Induced Effective Photoreduction of CO_2 to CO Catalyzed by Colloidal CdS Microcrystallites [1]

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Colloidal CdS microcrystallites prepared from $Cd(ClO_4)_2$ and H_2S in N,N-dimethylformamide catalyze effective and selective photoreduction of CO_2 to CO with apparent quantum yield, $\Phi_{1/2CO}$=0.098 (400 nm) using triethylamine as a sacrificial electron donor.

Photoreduction of CO_2 has attracted substantial attention as means for fuel production and resolving the global green house effect.[2] We recently reported that quantized ZnS microcrystallites with low density of surface defects[1] and oligo(*p*-phenylenes)[3] catalyze effective photoreduction of CO_2 to formate and/or CO under UV-light irradiation. With regard to visible-light induced photoreduction of CO_2 with CdS and related semiconductors, the formation of formic acid, and formaldehyde, or two-carbon products such as glyoxylic acid were reported but in low quantum yields and poor selectivity.[4] We have now found that colloidal CdS microcrystallites which can be readily prepared from $Cd(ClO_4)_2$ and H_2S in N,N-dimethylformamide (DMF) catalyze effective and selective photoreduction of CO_2 to CO with triethylamine (TEA) under >400-nm light irradiation.

Active colloidal CdS microcrystallites (CdS-DMF) were prepared as follows; 5 cm^3 of DMF solution of $Cd(ClO_4)_2.6H_2O$ (5×10^{-3} mol dm^{-3}) was taken into a Pyrex tube. After purging with argon gas, H_2S gas was introduced into the DMF solution under stirring on an ice bath, giving transparent colloidal CdS in DMF (CdS-DMF). CdS-DMF was used for photocatalysis after purging again with argon gas to remove unreacted H_2S. Fig. 1 shows the high-resolution transmission electron microscope of CdS-DMF. It has become clear that CdS-DMF is composed of hexagonal microcrystallites whose size ranges from 3 to 5 nm in diameter. Photoreduction of CO_2 was carried out as follows; CO_2 was introduced into a stirred DMF solution (2 cm^3) containing CdS-DMF (CdS diatomic concentration = 2.5×10^{-3} mol dm^{-3}) and TEA (1 mol dm^{-3}). The resulting CO_2 saturated DMF solution was closed with a rubber stopper, and then irradiated with a 300 W tungsten-halogen lamp through a sodium nitrite solution filter (>400 nm). The reaction was followed by GC, GLC, and HPLC.

As shown in Fig. 2, CdS-DMF catalyze efficient photoreduction of CO_2, leading to selective CO production without much H_2 evolution after short induction period. Diethylamine was detected as an oxidation product as usually observed when TEA was used as a sacrificial electron donor.[5] The reaction never occurred under dark or under illumination in the absence of CdS-DMF. In addition, highly pure commercially available bulk CdS(Furuuchi 99.999%, av. 2.5 μm), an active photocatalyst for the visible-light induced photoreduction of some aromatic ketones,[5)] was found inactive for the photoreduction of CO_2 under comparable conditions. These results suggest that size quantization effects contribute to the photoreduction of CO_2. $^{13}CO_2$ incorporation experiments with GC-MASS and ^{13}C-NMR revealed that ^{13}CO was formed but none of $H^{13}COOH$, $(^{13}COOH)_2$, $H^{13}CHO$, and $^{13}CH_3OH$ was detected in this system. These observations make clear that CdS-DMF-catalyzed photoreduction should lead to the selective formation of CO. It should be noted that solvent for preparation of CdS and reaction system plays a crucial role in the photoreduction of CO_2 as shown in Fig. 2; methanol (MeOH) and acetonitrile (AN) gave poor yields of CO. In DMF containing 1 v/v% water, the apparent quantum yield for the CO production was determined to be $\Phi_{1/2CO}$=0.098 at 400 nm. With addition of more than 10 v/v% water, the CO formation was decreased and the H_2 evolution was slightly increased.

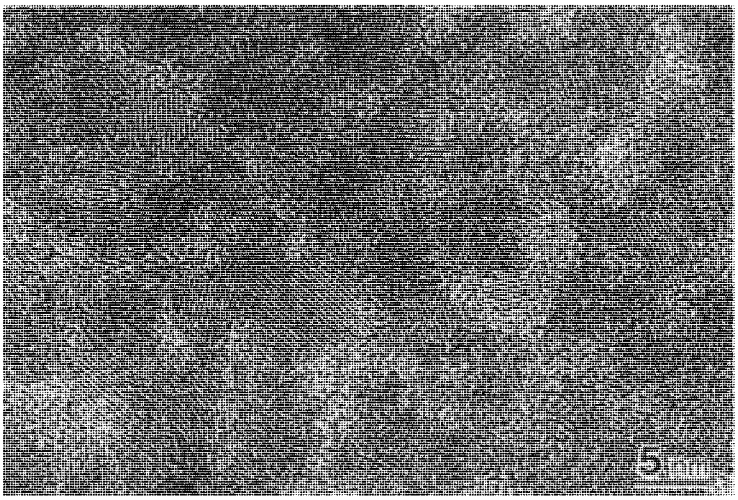

Fig.1 Transmission electron micrograph of CdS-DMF; Magnification 2300000 x

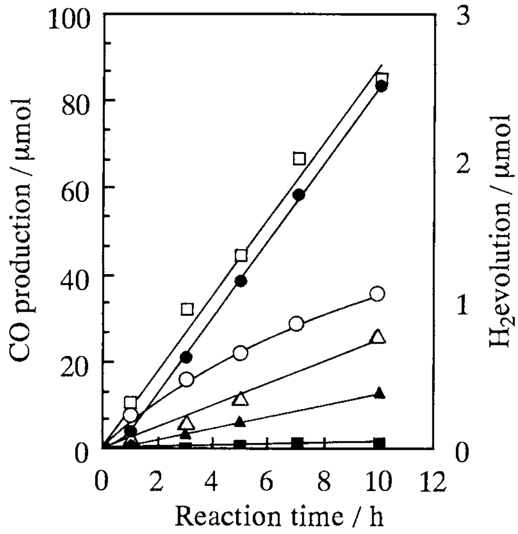

Fig.2 Visible-light-induced photoreduction of CO_2 catalyzed by CdS-DMF, (●) CO, (○) H_2; catalyzed by CdS-AN, (▲) CO, (△)H_2; catalyzed by CdS-MeOH, (■) CO, (□) H_2.

In conclusion, this is the first report of effective and selective photoreduction of CO_2 to CO catalyzed by colloidal CdS microcrystallites under visible-light irradiation.

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