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Effect of In^{3+} in Nano-Scale CdS-Catalyzed Photoreduction of CO_2 1)

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In^{3+}-modified hexagonal CdS nanocrystallites prepared from $Cd(ClO_4)_2.6H_2O$ and H_2S in N,N-dimethylformamide catalyze photoreduction of CO_2 in the presence of a small quantity of In^{3+} under visible light, leading to the competitive formation of $HCOO^-$ with CO without loosing the quantum yield for the CO_2 reduction obtained with unmodified hexagonal CdS nanocrystallites.

Photocatalytic reduction of CO_2 to useful organic molecules by using organic materials as electron donors can be regarded as equivalent to photosystem I (PS I) in the photosynthetic Z-Scheme, and photocatalysts and photosensitizers as key molecules for the artificial PS I have been investigated in view of efficiency and product selectivity.2) We have recently reported that CdS nanocrystallites prepared from $Cd(ClO_4)_2.6H_2O$ and H_2S in N,N-dimethylformamide (DMF) (CdS-DMF, 4-nm in diameter, hexagonal) catalyze efficient and selective photoreduction of CO_2 to CO ($\Phi_{1/2CO} = 0.098$) in the presence of triethylamine (TEA) as an effective electron donor under visible-light (λ>400-nm) irradiation.3) In general, surface conditions play a crucial role in photocatalysis with semiconductor nanocrystallites, because nano-scale crystallites consist of more than at least 70% surface elements.4) We attempted here to modify CdS-DMF nanocrystallites with transition metal ions, and have now found that modification with In^{3+} switches the reduction product from CO to $HCOO^-$ to an appreciable extent without loosing the total efficiency.

Active CdS nanocrystallites (CdS-DMF) were prepared as previously reported.3) Photoreduction of CO_2 was carried out as follows; 1 cm^3 of DMF solution containing TEA (2 mol dm^{-3}), $In(ClO_4)_3$ (0-2 mmol dm^{-3}), and 2 vol% of water, and 1 cm^3 of DMF solution containing CdS-DMF (CdS diatomic concentration = 5.0×10^{-3} mol dm^{-3}) were mixed in a Pyrex tube (8 mm in diameter). Into the resulting solution (2 cm^3), CO_2 was introduced under stirring. Irradiation and monitoring were conducted in the same way as reported.3)

As shown in Fig. 1, photoreduction of CO_2 with CdS-DMF proceed in the presence of In^{3+} (0.3 mmol dm^{-3}), giving not only CO but also $HCOO^-$ and H_2 after an induction period. $^{13}CO_2$ incorporation experiments coupled with GC-MASS and ^{13}C-NMR spectroscopy revealed that ^{13}CO (m/z = 29) and $H^{13}COO^-$ (δ = 168 ppm) were formed but none of $^{13}(COOH)_2$, $H^{13}CHO$, and $^{13}CH_3OH$ was detected in this system. These results clearly indicate that CO_2 was converted to CO and $HCOO^-$ on irradiation to the CdS-DMF/In^{3+}/TEA system. Diethylamine was detected as an oxidation product from TEA.1,3,5)

Figure 2 shows the dependence of product distribution on the In^{3+} concentration in the photocatalytic system. The $HCOO^-$ formation was increased with increasing the In^{3+} concentration to 0.3 mmol dm^{-3}, and then leveled off, while CO evolution was decreased continuously. In the system containing 0.3 mmol dm^{-3} of

In^{3+} ions, the apparent quantum yields for the formation of $HCOO^-$ and CO were determined to be $\Phi_{1/2HCOO^-} = 0.039$ and $\Phi_{1/2CO} = 0.061$, respectively. Interestingly, the sum of both quantum efficiency agrees with the quantum efficiency $\Phi_{1/2CO} = 0.098$ for the formation of CO obtained in the photoreduction in the absence of In^{3+}, suggesting the In^{3+}–modified surface should provide active sites for the product switching without loosing the total quantum yield.

The dramatic switch to the appreciable formation of $HCOO^-$ was ascribed to the surface modification of CdS–DMF with In^{3+} on basis of the following data and observation; 1) the addition of $In(ClO_4)_3$ did not affect the absorption spectrum of CdS–DMF in DMF within the examined range of concentration, 2) In^{3+} (6 coordination: r = 0.093 nm) is reported to have the similar ionic radius to Cd^{2+} (6 coordination: r = 0.109 nm), 3) the addition of $In(OH)_3$ prepared in DMF to the system showed the similar effects on the product distribution but none of the effects was observed for the addition of In_2S_3, 4) independent use of In_2S_3 prepared in DMF or comercially available $In(OH)_3$ as a photocatalyst did not lead to the reduction of CO_2 under the comparable conditions, 5) judging from the solubility of $In(OH)_3$ (4×10^{-23}) in water which is larger than that of In_2S_3 (4×10^{-78}) and CdS (5×10^{-28}), $In(OH)_3$ could contribute to the surface modification of CdS–DMF in aprotic polar solvent DMF.

Surface metal–ion modification of CdS–DMF was extended by using Ga^{3+} as homologous series of In^{3+}. However, the similar effect was not observed. Surface modification with Ni^{2+}, Co^{3+}, Fe^{3+}, and Cu^{2+} was also in vain. The addition of these transition metal ions resulted in the production of dark colored sulfides, because their solubility products are as small as that of CdS, and the photocatalysis of CdS–DMF should be inhibited (e. g., filter effect).

This is the first example of the surface modification aiming at effective product–control in the photocatalytic CO_2 reduction.

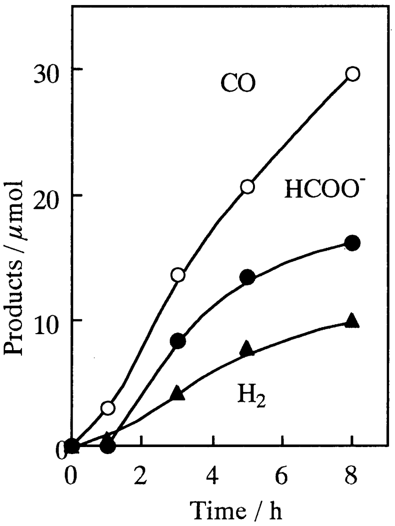

Fig. 1. CdS-DMF-catalyzed photoreduction of CO_2 in the presence of $In(ClO_4)_3$ (0.3 mM) and TEA.

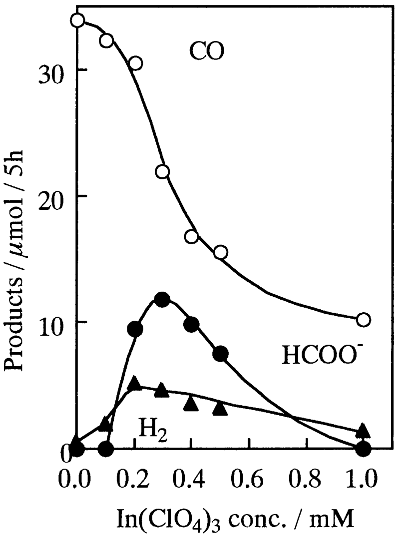

Fig. 2. Effect of $In(ClO_4)_3$ concentration on CdS-DMF-catalyzed photoreduction of CO_2 in the presence of TEA.

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