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PHOTOCATALYTIC HYDROGEN EVOLUTION FROM WATER USING ZINC SULFIDE AND SACRIFICIAL ELECTRON DONORS

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Irradiation($\lambda \geqq 290$ nm) of an aqueous suspension of ZnS prepared *in situ* from Na_2S and $ZnCl_2$ or $ZnSO_4$ leads to the photocatalytic H_2 evolution in the presence of sacrificial electron donors such as tetrahydrofuran, methanol, and ethanol.

From the viewpoint of solar energy utilization, photocatalysis of semiconductors has been intensively studied during the last few years. It was recently shown that the combination with redox noble metal catalysts was indispensable for the efficient transfer of photoinduced valence band holes and conduction band electrons1) and for the protection against photocorrosion of semiconductor.2) The photolysis of water using zinc sulfide, however, had drawn little attentions because zinc sulfide is photodegradable in water.3) We report here that, without the combination with any redox catalysts, the freshly prepared colloidal zinc sulfide is fairly efficient in the photocatalytic cleavage of water in the presence of some electron donors.

In a typical experiment, equimolecular amounts of zinc chloride and sodium sulfide nonahydrate(Special grade of Wako Pure Chemical Industries, Ltd.) were precisely weighed(each 0.12 mmol ± 5 %) and placed in a 30-ml Pyrex tube. Doubly distilled water(7 cm^3) was pipetted into the above tube, causing a colloidal suspension of ZnS. Into this was further pipetted tetrahydrofuran(THF)(1 cm^3) as an electron donor. The reaction mixture was purged with argon gas, evacuated, placed nearest to a 125 W high-pressure Hg arc lamp, and then irradiated at 25°C with vigorous stirring. After irradiation($\lambda \geqq 290$ nm), the internal pressure was brought to atomospheric pressure by injecting water into the reaction tube. The gas produced was analyzed by gas chromatography and mass spectrometry.

The main gaseous product was H_2 and the amount of H_2 generated increased linearly with the elapse of time during 22 h irradiation(the rate(25°C): 0.50 cm^3 H_2/h). The turnover number of the catalyst went up to 3.3 mmol H_2/mmol cat. after 22 h irradiation(12.0 cm^3 of H_2 was evolved). Further irradiation, however, was accompanied by a slight decrease in the rate of H_2 evolution. Although the catalyst turned slightly grey, no appreciable degradation was confirmed.4)

In order to clarify the source of hydrogen atoms, UV irradiation was performed in the presence of D_2O using zinc chloride and sodium sulfide deuterononahydrate. The average D_2/DH ratio in the mass spectrum was 7.09, indicating that hydrogen was formed by the cleavage of the bulk water.

Table. Photocatalytic Hydrogen Production from Water-Electron Donor Mixture Using Zinc Sulfide[a)]

	colloidal ZnS							commercial	
	from $ZnCl_2$	from $ZnSO_4$	from $ZnCl_2$	from $ZnSO_4$	from $ZnSO_4$	from $ZnSO_4$	from $ZnSO_4$	ZnS	$ZnS^{b)}$
sacrificial electron donor	THF	THF	MeOH	MeOH	EtOH	*i*-PrOH	TEA	THF	THF
irradiation time/h	22	20	15	18	18	21	12	19	17
hydrogen/mmol	0.49	0.72	0.23	0.36	0.54	0.21	0.023	0.004	0.003
turnover number/ mmol H_2/mmol cat.	3.30	4.06	1.77	3.04	4.78	1.57	0.16	0.03	0.34

a) Initial composition: H_2O 7 cm^3, electron donor 1 cm^3, ZnS 0.1-0.2 mmol.
b) ZnS 0.01 mmol was used. c) TEA=triethanolamine.

The formation of CO_2 was negligible even after prolonged irradiation. CO, H_2S, and O_2 were not observed. GC-mass analysis of the liquid products indicated the presence of dimeric THF and some oligomeric products as oxidized products.

As shown in the Table, zinc sulfide prepared from zinc sulfate heptahydrate (Special grade of Wako Pure Chemical Industries, Ltd.) was also active in the photolysis, while commercial zinc sulfide(Mitsuwa Pure Chemicals' electronic luminescent grade) showed the weak activity. H_2 was also produced fairly efficiently in the presence of methanol, ethanol, or 2-propanol as a sacrificial organic donor.

As previously reported,[3)] irradiation of colloidal zinc sulfide in the absence of sacrificial electron donors led to the apparent degradation of the catalyst, i.e., the catalyst turned black progressively with an evolution of a small quantity of H_2. On the other hand, Stephens et al[5)] reported that zinc sulfide is a fair photocatalyst for the reduction of O_2 to H_2O_2 in the presence of phenol, and that the catalytic activity depends strongly on the preparation methods. The present findings may indicate that the colloidal zinc sulfide prepared *in situ* should facilitate the transfer of photoinduced conduction band electrons and valence band holes to the bulk water and the appropriate donor, respectively.

References

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