Journal of

The Chemical Society,

Chemical Communications

NUMBER 4/1981

Photochemical Hydrogen Production using Cadmium Sulphide Suspensions in Aerated Water

By JAMES R. DARWENT* and GEORGE PORTER

(*Davy Faraday Research Laboratory, The Royal Institution, 21 Albemarle Street, London* W1X 4BS)

Summary Suspensions of CdS particles sensitize the photoreduction of H_2O by cysteine and ethylenediaminetetra-acetic acid with a quantum yield of 0·04 mol/einstein (λ = 436 nm); this yield is only marginally reduced in the presence of oxygen.

IN recent years considerable interest has focused on the development of systems to convert solar energy into useful chemical potential.[1] One of the most attractive would involve the photodecomposition of H_2O into O_2 and H_2 with visible light. Significant progress has been achieved using homogeneous photoredox reactions with microheterogeneous catalysts.[2] A typical system contains sensitizer [Ru(2,2′-bipyridyl)$_3^{2+}$], electron relay (methyl viologen, MV^{2+}), and redox catalyst (Pt or RuO_2). An alternative approach involves totally heterogeneous systems for the photoelectrolysis of H_2O.[3]

Rapid reaction of O_2 with the reduced electron relay (MV$^{\cdot+}$) imposes a severe limitation on the efficiency of homogeneous systems. This problem can be reduced if the sensitizer, relay, and catalyst are closely linked. One of the simplest ways of achieving this is to adsorb a catalyst on to a semiconductor surface. If a low band gap (<2·5 eV) semiconductor is chosen, it can be excited by visible light to provide an electron–hole pair which replaces the conventional redox relay. In an ideal system, e$^-$ and h$^+$ would migrate to respective catalysts on the semiconductor surface and liberate both H_2 and O_2. Such systems are likely to be inefficient owing to rapid recombination of the charges, this being particularly favourable under the potential required to electrolyse H_2O (>1·23 V). An alternative approach could involve two photocycles with a linking redox couple (at a potential such that reaction with O_2 is unfavourable). As a first approach to such a system we have investigated the photoreduction of H_2O using electron donors such as ethylenediaminetetra-acetic acid (EDTA) and cysteine. Such compounds have been well studied in homogeneous model systems[2f,4] where they are irreversibly oxidized.

CdS suspensions have been previously shown to photosensitize the reduction of O_2 and MV^{2+} by EDTA.[5] This semiconductor has a band gap of 2·4 eV and absorbs light strongly below 510 nm. CdS particles were platinized by precipitation of colloidal Pt. For a typical photolysis experiment CdS powder (5 mg) was stirred and illuminated in a 10 mm cuvette. The pH was maintained at 6·2 with 0·1 M phosphate buffer. CdS (99·999%) (Koch-Light), EDTA (B.D.H.), and K_2PtCl_6 (B.D.H.) were used as supplied. H_2O was doubly distilled. Colloidal Pt was prepared by reduction of K_2PtCl_6 with sodium citrate,[6] followed by stirring with an ion exchange resin to remove the citrate. This sol was then stirred for 12 h with CdS powder after which the solid was filtered off, washed, and dried. Quantum yields were measured using a ferrioxalate actinometer[7] and gases were analysed by g.l.c.

When illuminated with light (λ >360 nm) in the presence of EDTA or cysteine CdS particles photosensitize the reduction of H_2O. Yields of H_2 increase dramatically when platinized CdS particles are used as shown in the Figure. More interestingly, the evolution of H_2 is also observed when samples are not purged with N_2 and are equilibrated with 2 ml of air above the solution. As shown in the Figure, there is surprisingly little change in the rate of H_2 evolution under these aerobic conditions. For a 2 h period the quantum yield of H_2 was found to be 0·04 mol/einstein (λ 436 nm). This quantum yield should be seen as a lower limit as it has been assumed that all the photons reaching the sample are absorbed and no allowance was made for

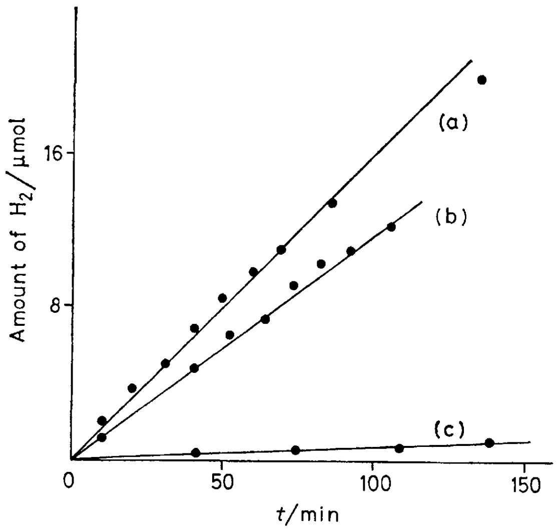

FIGURE. H_2 evolution from 5 ml samples containing 0·1 M EDTA and 0·1 M phosphate buffer (pH 6·2) when irradiated with visible light (λ >360 nm). Solutions for curves (a) and (b) contain 5 mg of platinized CdS, (c) contains 5 mg of CdS. Trace (b) was obtained for an air-equilibrated solution.

the considerable amount of light reflected and scattered by the particles. No H_2 was evolved in the absence of sacrificial electron donors or when samples were not illuminated. Prolonged irradiation (>4 h) was accompanied by the decomposition of the semiconductor and a pronounced decrease in the rate of H_2 formation.

These observations correlate well with the extensive literature available for CdS liquid junction solar cells.[8] Absorption of light promotes electrons into the conduction band of CdS, where the potential (−0·9 V) (*vs.* standard calomel electrode, S.C.E.) is sufficient to reduce water in the presence of a Pt catalyst [$E(H^+/\frac{1}{2}H_2)$ = −0·61 V *vs.* S.C.E. at pH 6·2]. Holes in the valence band are at a high positive potential (1·5 V *vs.* S.C.E.)[8b] and in the absence of alternative electron donors can oxidize CdS ($E_{\text{decomp.}}$ = 0·08 V *vs.* S.C.E.).[8b] This process may be kinetically slow and alternative electron donors can compete and effectively stabilise the semiconductor, polysulphide and polyselenide redox couples being particularly favourable.[9] In the present case EDTA and cysteine appear to stabilise CdS inefficiently. Alternative electron donors may overcome this problem, while improved H_2-evolving catalysts should increase the quantum yield for H_2 formation.

Finally, the quantum yield for H_2 formation (0·04 mol/einstein) compares unfavourably with the value of 0·3 mol/einstein recorded recently in our laboratory for a system using zinc(II) tetra(*N*-methylpyridyl)porphyrin as photosensitizer with MV^{2+} as electron relay.[2g] However, such schemes are restricted to anaerobic conditions, whereas the present system operates with moderate efficiency in the presence of air. Additionally, the present system is at an early stage and improved yields may be obtained under optimized conditions.

We thank the members of the Davy Faraday Research Group for their encouragement during this work which was supported by the S.R.C.

(*Received, 6th November* 1980; *Com.* 1199.)

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