Visible Light Induced Generation of Hydrogen from H_2S in Mixed Semiconductor Dispersions; Improved Efficiency through Inter-particle Electron Transfer

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Electron transfer from the conduction band of CdS to that of TiO_2 particles occurs in alkaline suspensions containing SH^- ions and is exploited to improve the performance of a system that decomposes H_2S with visible light.

Light induced charge separation constitutes an important step in the conversion of photons into chemical energy by natural or artificial photosynthetic devices. To obtain good efficiencies, provisions must be made to avoid back reactions of charge carriers, *i.e.* oxidized and reduced species, formed in the primary photoredox event. The present note introduces inter-particle electron transfer between two different types of semiconductors as a new strategy to accomplish vectorial displacement of charges and avoid electron–hole recombination. A first successful application involves the visible light induced decompostion of H_2S into hydrogen and sulphur.

CdS (Fluka, purissimum, 99.999%) and Al_2O_3–C (Degussa) were used as supplied and anatase (145 m^2/g, elementary particle size *ca.* 100 Å, doped with 600 p.p.m. Nb) was kindly provided by Dr. P. Panek, Bayer GmbH, West Germany. Other chemicals were at least reagent grade and

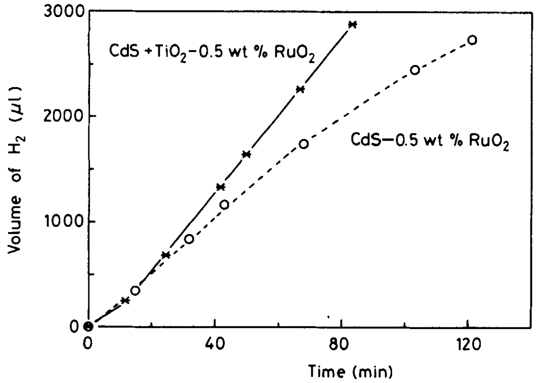

Figure 1. Volume of hydrogen (S.T.P.) produced by visible light irradiation of two CdS dispersions. In one case the RuO_2 is directly loaded (wt %) onto CdS particles (dashed line); in the other case TiO_2 particles are loaded with the same amount of RuO_2 and naked CdS is excited by light (solid curve). Other conditions as in Figure 2.

used as received. RuO_2 loading of CdS was carried out by impregnating the powder with the desired amount of aqueous $RuCl_3$ solution, while adding a few drops of concentrated HCl during the mixing. The slurry was then dried and calcined in air for 1 h at 320 °C to form the ruthenium oxide. An analogous procedure was applied for RuO_2 loading of TiO_2 except that no HCl was admitted during the mixing. Platinum sol was prepared from H_2PtCl_6 by citrate reduction.[1] The colloidal solution obtained was decitrated with Amberlite MG3 ion exchange resin until the conductivity was below 15 µS/cm. The Pt sol was mixed with CdS or TiO_2 and dried at 130 °C for 1 h. The loading was 0.5 wt % in each case. Irradiations were carried out with samples of 25 ml volume contained in a pyrex glass vial closed with a septum. Solutions contained invariably 0.1 M Na_2S, 1 M NaOH, and 50 mg CdS. Experiments with mixtures employed, in addition to CdS, 50 mg/25 ml TiO_2 or Al_2O_3. Prior to irradiation the suspensions were purged with Ar for *ca.* 15 min. A 450 W Xe lamp equipped with a water jacket and a 400 nm cut-off filter to remove i.r. and u.v. radiation, respectively, was used as a light source. The integral irradiance ($\lambda > 330$ nm) of this lamp was determined as 160 mW/cm^2. Hydrogen was detected by gas chromatography using a Carbosieve 5 Å column and Ar as carrier gas. Light absorption by the 0.5 wt % Pt loading is not significant; light is absorbed by polysulphides formed during the photoreaction the result of which shows in Figure 1 as a negative deviation in the hydrogen formation curve for CdS–0.5 wt % RuO_2.

Figure 2 shows the volume of H_2 produced by visible light irradiation of different CdS dispersions as a function of irradiation time. Initial rates of H_2 generation [$r(H_2)$] are listed in Table 1. Naked CdS particles produce H_2 at a rate of 0.41 ml/h. Addition of Al_2O_3 leads to a small increase in $r(H_2)$ while TiO_2 decreases it by more than a factor of two. H_2 generation is almost totally suppressed by Pt loaded TiO_2 particles, $r(H_2)$ amounting to only 54 µl/h. Replacement of Pt on the TiO_2 particles by RuO_2 results in a striking 42-fold increase in the rate of H_2 generation to a value of 2.23 ml/h. In fact, the efficiency of this system is superior to that where RuO_2 is directly deposited onto the CdS particles.[2] This is clearly demonstrated in Figure 1 where hydrogen evolution curves obtained for RuO_2-loaded CdS and a mixture of CdS with RuO_2-loaded TiO_2 are compared. The latter catalyst gives higher H_2 yields and the rates are better sustained when compared to CdS–RuO_2 under identical experimental conditions. Results from a mixture of naked TiO_2 with a suspension of RuO_2-loaded CdS particles are included in Figure 2. The effect of TiO_2 is to decrease slightly the value of $r(H_2)$ observed with CdS–RuO_2 alone. Finally, Table 1 mentions an important blank experiment where TiO_2–RuO_2 dispersions were irradiated by visible light in the absence of CdS. Only minute amounts of H_2 could be detected in this case [$r(H_2)$ *ca.* 5 µl/h].

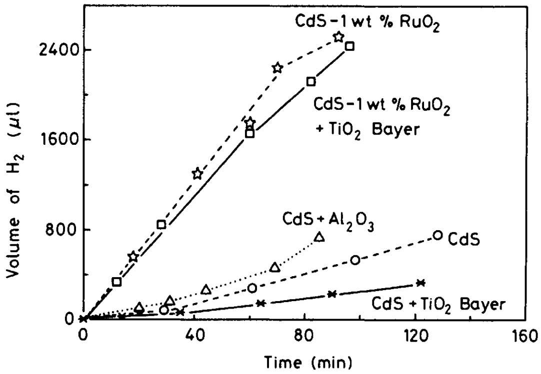

Figure 2. Volume of hydrogen (S.T.P.) produced by visible light irradiation of various CdS dispersions as a function of irradiation time. *Conditions*: *T ca.* 40 °C, 0.1 M Na_2S–1 M NaOH, CdS and TiO_2 (or Al_2O_3) present at 50 mg each/25 ml solution. The curve for Al_2O_3–CdS was determined to check the (trivial) effect of light scattering on the hydrogen yield.

Table 1. Initial rates of H_2 production with semiconductor dispersions with different compositions.[a]

Dispersion	$r(H_2)$, ml/h
CdS	0.41
CdS + TiO_2	0.19
CdS + Al_2O_3	0.45
CdS–Pt (0.5 wt %)	0.60
CdS–RuO_2 (0.5 wt %)	1.57
CdS–RuO_2 (1.0 wt %)	1.86
CdS–RuO_2 (1.0 wt %) + TiO_2	1.66
CdS + TiO_2–RuO_2 (0.5 wt %)	2.23
CdS + TiO_2–Pt (0.5 wt %)	0.05
TiO_2–RuO_2 (0.5 wt %)	0.00

[a] *Conditions*: semiconductor dispersion in 0.1 M Na_2S–1 M NaOH, each semiconductor material present at 50 mg/25 ml solution, *T ca.* 40 °C, visible light ($\lambda > 400$ nm) irradiation. Reproducibility from batch to batch made under identical conditions is better than 20%.

These observations are rationalized as follows: light is absorbed by the CdS particles producing electron–hole pairs, equation (1). Holes react with hydrogen sulphide ions to give sulphur which dissolves as polysulphide in solution [equation (2)]. The complementary reaction of conduction band electrons, competing with electron–hole recombination, is reduction of water to hydrogen. In the semiconductor dispersions reported here, this process can occur *via* different pathways depending on the composition of the systems: (i) *direct reduction of water by e^-_{CB} (CdS)*. This mechanism, equation (3), operates in naked CdS dispersions in the absence of TiO_2. Although CdS is a poor catalyst for H_2 generation when compared to noble metals,[2a] cleavage of H_2S proceeds with reasonable efficiency, since the driving force for H_2 generation is high [*ca.* 250 mV, based on a value of −1.05 V *vs.* normal hydrogen electrode (N.H.E.) for the conduction band position of CdS in 0.1 M Na_2S[3]]. (ii) *Redox catalyst assisted reduction of water by e^-_{CB} (CdS)*. In this case water reduction is obtained when the conduction band electron is first trapped by the catalyst (Pt, RuO_2) deposited onto the CdS particles. From the $r(H_2)$ values presented in Table 1 the effect of Pt is small while RuO_2 accelerates markedly the hydrogen generation rate. (iii) *Inter-particle electron transfer from CdS to TiO_2.* The driving force for reaction (4) is 180 mV, based on a conduction band potential of −870 mV (*vs.* N.H.E.) for anatase particles at pH 14.[4] Once trapped by TiO_2 particles, conduction band electrons can still generate hydrogen, reaction (5).

$$CdS \underset{\text{Heat}}{\overset{h\nu}{\leftrightarrows}} e^-_{CB}(CdS) + h^+(CdS) \qquad (1)$$

$$2h^+ + SH^- \rightarrow S + H^+ \qquad (2)$$

$$2e^-_{CB}(CdS) + 2H_2O \rightarrow H_2 + 2OH^- \qquad (3)$$

$$e^-_{CB}(CdS) + TiO_2 \rightarrow e^-_{CB}(TiO_2) + CdS \qquad (4)$$

$$2e^-_{CB}(TiO_2) + 2H_2O \rightarrow H_2 + 2OH^- \qquad (5)$$

However, on naked TiO_2 this reaction is slow and an efficient redox catalyst is needed to promote water reduction for which the driving force is only *ca.* 50 mV. Thus, it is not surprising that addition of naked TiO_2 to CdS suspensions decreases the efficiency of photoinduced H_2 generation. A small decrease is even noted when TiO_2 is added to RuO_2-loaded CdS which indicates that inter-particle electron transfer can compete with trapping of e^-_{CB} by the RuO_2 deposit. Of the two redox catalysts used here in conjuction with TiO_2, Pt has a deleterious effect on the H_2 yields suppressing H_2 evolution almost totally. This behaviour is attributed to the blocking of active sites of the catalyst by SH^- ions present in the solution. As a consequence, the Pt deposit, whilst still acting as a trap for conduction band electrons, is rendered inoperative for H_2 generation at the low overpotential that is available. The striking improvement in the efficiency of H_2S cleavage observed when RuO_2 instead of Pt is deposited onto the TiO_2 particles indicates that the problem of inactivation of catalytic sites by SH^- does not exist with this material. Equally important is the finding that the performance of the system containing CdS in combination with TiO_2–RuO_2 is better than that of CdS–RuO_2 alone. (Based on the heat of combustion of H_2 and the *total incident* light energy, we calculate for the former system an overall energy conversion efficiency of 1%). This leaves no doubt that through the combination of these two semiconductor materials the extent of electron–hole recombination is reduced. Charge separation is achieved through selective transfer of conduction band electrons from CdS to TiO_2 particles, the transfer of holes between valence bands being inhibited for energetic reasons.

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