

Improvement of the Photoelectrochemical Change of H₂S over CdS Suspensions using RuS₂ as a Catalyst

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Illumination of a suspension of CdS particles loaded with 0.5 wt% RuS₂ leads to photocatalytic H₂ evolution from alkaline S²⁻/SO₃²⁻ solutions with a formal quantum efficiency of 0.12 at 470 nm; in comparison with the analogous system, CdS/0.5 wt% RuO₂, this represents an improvement by a factor of 7.

CdS with a bandgap of 2.4 eV absorbs light strongly below 520 nm and is therefore an attractive material for photoelectrochemical (PEC) purposes using solar light. Upon illumination with visible light, aqueous suspensions of CdS particles loaded with RuO₂ catalyst cleave H₂S into H₂ and S (polysulphide).¹ H₂ is also photocatalytically produced over dispersions of CdS particles loaded with small deposits of either Pt or RuO₂ with the sacrificial oxidation of ethylenediaminetetra-acetic acid (EDTA),² a sulphite,³ etc. Recently, it has been shown that addition of a sulphite makes the cleavage of H₂S more efficient, because the sulphite serves as a sink for the S atoms formed yielding a thiosulphate.⁴ Photocatalytic H₂ evolution from an aqueous solution of a sulphide is not significantly improved when CdS is loaded with Pt and RuO₂.¹

The present report deals with the design and operation of a new photocatalytic system, *viz.* CdS loaded with RuS₂. The choice of RuS₂ is prompted by the fact that among the transition metal sulphides RuS₂ has proven to be the best catalyst for the hydrodesulphurisation of fused thiophenes.⁵ Moreover, in view of the sulphidic environment, RuS₂ is likely to be a better catalyst for the present reaction than RuO₂. Recently, attempts to grow single crystals of RuS₂ have been successful.^{6,7} From PEC measurements it has been shown that on RuS₂, a semiconductor with a bandgap of 1.8 eV, transfer of holes takes place from the valence band to water, thus producing oxygen.⁶ RuS₂ is a promising material because of its stability towards corrosion, in contrast with other transition metal sulphides. In this note we report the catalytic properties of RuS₂ in comparison with RuO₂ for H₂S cleavage over CdS dispersions.

CdS/0.5 wt% RuO₂ was prepared as described previously.^{4a} CdS/0.5 wt% RuS₂ was prepared as follows. A solution of NaHS (Ventron) (7.55 mg) in H₂O (5 ml) was added to a suspension of K₂RuCl₆ (Ventron, Ru = 26%) (11.91 mg) and CdS (Fluka, 99.999%) (1g) in H₂O (10 ml) under nitrogen. The suspension was stirred for 4 h at 22 °C, dried, and heat-treated in pure H₂S (Baker) at 250 °C for 1.5 h. The activity of the RuS₂ catalyst strongly depends on the method of preparation employed (starting materials, solvent, annealing conditions). The procedure given here produces the catalyst with the highest photocatalytic activity.

Figure 1 shows the PEC generation of H₂ over CdS/0.5 wt% RuS₂ and CdS/0.5% RuO₂ from three substrates, *viz.* EDTA, S²⁻, and S²⁻/SO₃²⁻, as a function of the illumination time. Yields of hydrogen are substantially augmented when RuS₂ is used as a catalyst instead of RuO₂. Both in the presence of RuS₂ and RuO₂ addition of SO₃²⁻ to S²⁻ results in a considerable increase in H₂ evolution, whereas H₂ formation from H₂O reduction is less efficient, when a donor like EDTA is sacrificed. As shown previously, the rate of H₂ generation decreases upon prolonged illumination of an aqueous solution of S²⁻/SO₃²⁻ over CdS/RuO₂.^{4a} However, no loss of activity is observed after 25 h using CdS/RuS₂.

Figure 2 shows the rate of H₂ evolution $r(\text{H}_2)$ from S²⁻/SO₃²⁻ over CdS/0.5 wt% RuS₂ as a function of the

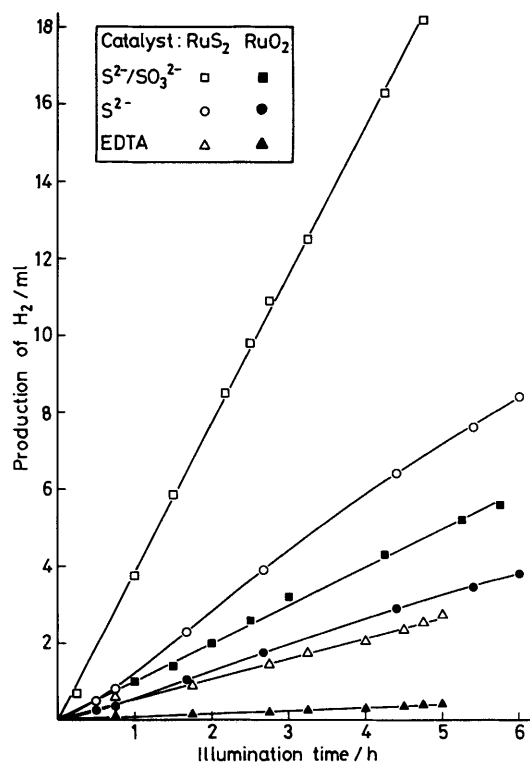


Figure 1. H₂ production as a function of the illumination time. System 75 mg CdS/0.5 wt% cat/75 ml; pH 13, 40 °C; 700 W high-pressure mercury lamp (Hanau, $\lambda > 418$ nm). The quantity of hydrogen produced was measured volumetrically. All substrate concentrations 0.1 M.

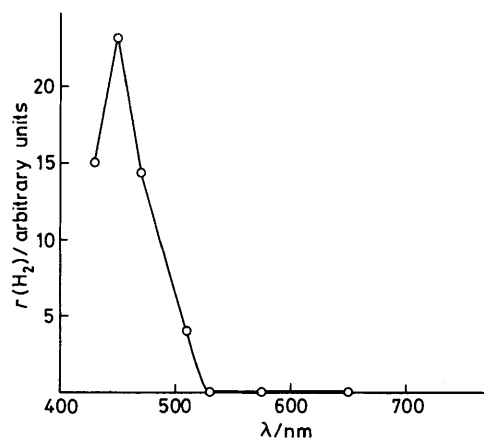


Figure 2. Rate of H₂ production $r(\text{H}_2)$ over CdS/0.5 wt% RuS₂ particles (75 mg/75 ml) in aqueous suspension upon illumination ($\lambda > 418$ nm) at pH 13 and 40 °C as a function of wavelength (corrected to constant energy). [S²⁻] = [SO₃²⁻] = 0.1 M. H₂ analysed by g.c. For further details, *cf.* ref. 8.

wavelength of the incident light. Clearly, the wavelength dependence reflects the light absorption properties of CdS thereby excluding the possibility of a significant contribution by PEC processes resulting from direct excitation of RuS₂. Above ca. 520 nm no excitation of electrons into the conduction band occurs. Below the maximum (ca. 450 nm) the incident light penetrates less deeply into the material and surface recombination becomes the predominant process. We have determined the formal quantum efficiency Φ , defined in equation (1). At 470 nm, where $r(\text{H}_2)$ reaches about two thirds of its maximum value (at λ ca. 450 nm), we find a value for Φ of 0.12. Under identical conditions we have found a value for Φ of 0.018 at 470 nm for CdS/0.5 wt% RuO₂. Both values correspond to lower limits for the true quantum yields. The use of RuS₂ instead of RuO₂ gives a sevenfold increase in efficiency. The Φ value of 0.12, obtained at 470 nm, is of approximately the same order of magnitude as the value reported for a system based on CdS/1% Pt.⁹ In that case the CdS particles had undergone a special pretreatment, viz. photoetching, prior to use in PEC experiments.

Further details on different preparation methods of RuS₂ and characterisation of the resulting products will be published elsewhere, as well as the activities of the various CdS/RuS₂ materials in PEC processes in relation to their structures and surface properties.

$$\Phi = \frac{\text{number of atoms of H}}{\text{number of incident photons}} \quad (1)$$

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