Photocatalytic H_2 and O_2 Generation from Water Using a CdS Dispersion Loaded with Pt, Ir, or Rh and RuO_2. Use of $[\{Ru(OH)(edta)\}_2(O_2)]$ as an Electron Relay (H_4edta = Ethylenediaminetetra-acetic Acid)

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The μ-peroxo-ruthenium(IV)-dioxygen complex $[\{Ru(OH)(edta)\}_2(O_2)]$ (H_4edta = ethylenediaminetetra-acetic acid) acts as an electron relay in a photochemical hydrogen and oxygen generating system with loaded CdS dispersion.

The generation of hydrogen from water using visible light in the presence of colloidal semiconductors is currently a topic of extensive investigations.[1—4] It was shown that[5,6] loading of the semiconductor dispersion with noble metal catalysts is essential for the efficient transfer of photoinduced valence band holes and conduction band electrons and for protection against photocorrosion of the semiconductor. Much of the work has been done on TiO_2 particles, and ZnS[7] and WO_3 loaded with Pt and RuO_2. The presence of RuO_2 in these systems drastically increases the quantum yield of H_2 and O_2 under band gap irradiation.[8,9]

CdS is a colloidal semiconductor with a band gap[3] of 2.4 eV.

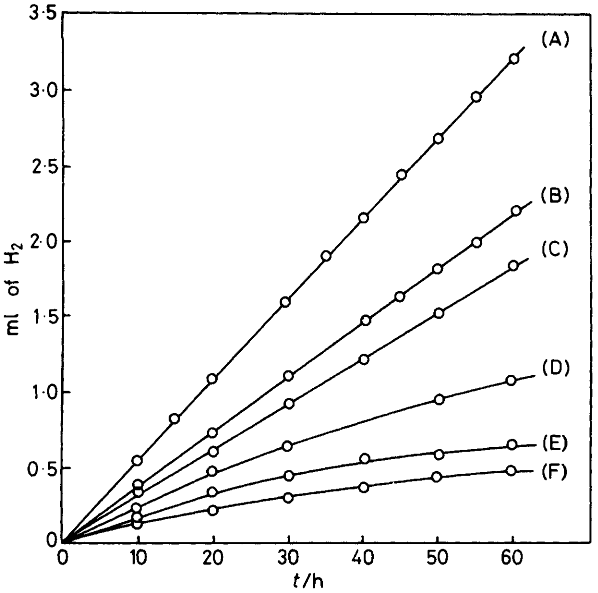

Figure 1. Rate of hydrogen production from water under illumination by visible light. (A) $CdS/Rh/RuO_2$, (B) $CdS/Pt/RuO_2$, and (C) $CdS/Ir/RuO_2$ in the presence of (**1**); (D) $CdS/Rh/RuO_2$, (E) $CdS/Pt/RuO_2$, and (F) $CdS/Ir/RuO_2$ in the absence of (**1**).

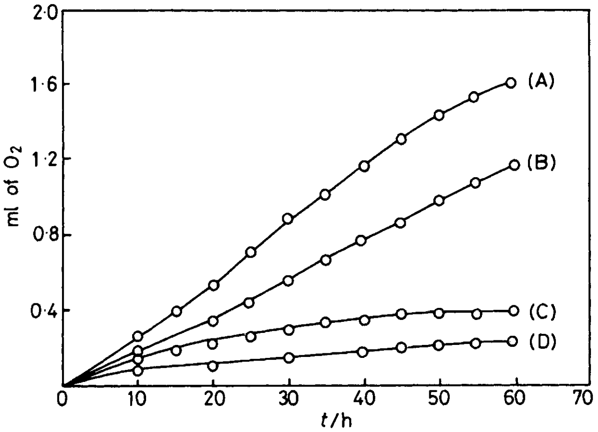

Figure 2. Rate of oxygen production from water under illumination by visible light. (A) $CdS/Rh/RuO_2$ and (B) $CdS/Pt/RuO_2$ in the presence of (**1**); (C) $CdS/Rh/RuO_2$ and (D) $CdS/Pt/RuO_2$ in the absence of (**1**).

Grätzel *et al.*[9] reported water cleavage in a CdS dispersion loaded with Pt and RuO_2. There was a considerable enhancement in H_2 evolution when edta (H_4edta = ethylenediaminetetra-acetic acid) was added as a sacrificial donor which was irreversibly oxidized during the photoreduction of water. Very few examples are known[1,4,10] of systems in which the electrons from the conduction band reduce water to form H_2 and the positive holes from the valence band oxidize water to form O_2. The problem encountered in these systems is the availability of a suitable electron relay to catalyse the hole oxidation of OH^- to generate O_2.

We report here the splitting of water by visible light using colloidal CdS particles loaded with Pt, Rh, or Ir and RuO_2 in the presence and absence of the electron relay[11] $[\{Ru(OH)(edta)\}_2(O)_2)]$ (**1**). The enhancement in the rate of H_2 production, the role of (**1**) as a relay, and the mechanism of H_2 and O_2 production in the system are reported.

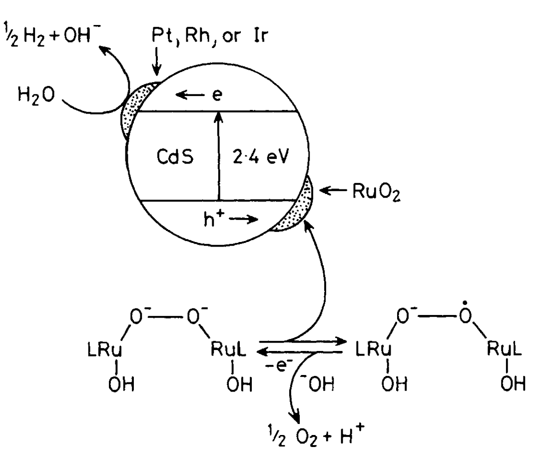

Figure 3. Mechanism of the photoreduction of water in the presence of complex (**1**) as electron relay (L = edta).

$[\{Ru(OH)(edta)\}_2(O_2)]$
(**1**)

Pt, Rh, or Ir and RuO_2 were loaded on CdS particles by the method of photodeposition.[10] The catalyst $CdS/Pt/RuO_2$, $CdS/Ir/RuO_2$, or $CdS/Rh/RuO_2$ (50 mg) was suspended in water (10 ml) in a Pyrex cell (20 ml) and illuminated by a 450 W xenon lamp through a 400 nm cut-off filter and a 5 cm capacity water cell to eliminate u.v. and i.r. radiation. The samples were deaerated prior to the illumination by flushing with nitrogen and the solution pH was adjusted to 7.6. The oxygen evolved was absorbed in a solution of alkaline pyrogallol and the H_2 analysed using a molecular sieve 5 Å column and argon as a carrier gas. The experiments were repeated in the presence of 0.1 M $[\{Ru(OH)(edta)\}_2(O_2)]$ (**1**) at pH 7.6. The results of H_2 evolution in the presence and absence of (**1**) are shown in Figure 1. The rate of hydrogen evolution decreases in the order $CdS/Rh/RuO_2 > CdS/Pt/RuO_2 > CdS/Ir/RuO_2$. For the catalyst $CdS/Rh/RuO_2$ the rate of H_2 evolution was 60 and 20 $\mu l\ h^{-1}$, respectively, in the presence and absence of (**1**). In order to measure the amount of oxygen generated, the mixture of gases was passed through alkaline $KMnO_4$ solution where the hydrogen was absorbed and the residual gas was analysed using the method described earlier.[12] The rate of O_2 evolution was 31 and 9 $\mu l\ h^{-1}$, respectively, in presence and absence of complex (**1**) in the case of the $CdS/Rh/RuO_2$ catalyst. The O_2 generation results are shown in Figure 2. For the other catalysts, $CdS/Pt/RuO_2$ and $CdS/Ir/RuO_2$, the rate of H_2 and O_2 evolution was increased by 2—2.5 times in the presence of (**1**). A blank experiment in which only complex (**1**) was illuminated showed no evolution of H_2 or O_2. The irradiation of CdS/Pt, CdS/Ir, and CdS/Rh in the absence of RuO_2 also did not show any measurable quantity of gas evolution in either the presence or absence of complex (**1**). The photocorrosion of CdS was observed in the form of free sulphur. The dioxygen complex (**1**) and the catalysts were recovered unchanged from the reaction system by centrifuging at 20,000 r.p.m. The catalyst can be used after vacuum drying without any loss in activity. The concentration of the dioxygen complex (**1**) before and after the experiment was checked by its characteristic ligand-to-metal charge-transfer absorption peak at 390 nm ($1\pi^*O_2 \rightarrow d\sigma\ Ru^{IV}$). The dioxygen complex was completely intact after 70 h of experiments. The system is highly pH dependent with an optimal H_2 evolution in the pH range 7.6—8.50, the range in which complex (**1**) is stable.

In these systems RuO_2 acts as fast hole scavanger and Pt, Ir, or Rh acts as catalyst[9] for transfer of electrons from the conduction band of CdS to H_2O producing H_2. The enhancement in H_2 and O_2 production in the presence of (**1**) may be due to the transfer of an electron from the peroxo group of (**1**) to the hole in the valence band of CdS *via* RuO_2. At the present stage of investigation it cannot be said whether (**1**) forms a loose complex with RuO_2. A loose surface peroxo complex was reported[13] in the O_2 generation system with TiO_2 dispersion. The superoxo species formed after the transfer of electron to the hole is a very strong oxidizing agent and oxidizes OH^- to O_2 and H^+ being reduced itself to the peroxo complex (**1**). The mechanism is shown in Figure 3.

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