Photogalvanic generation of dihydrogen by water splitting using MoS_4^{2-} as catalyst

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Abstract. A 4% solar energy efficiency has been achieved for photogeneration of dihydrogen (H_2) using MoS_4^{2-} as catalyst, when the anode compartment of a photogalvanic cell is illuminated. The generated photocurrent rises slowly with time and reaches a limiting value. Ten hours after the reaction starts, a secondary dark reaction sets in which produces H_2 and photocurrent even when the light is switched off. Possible mechanisms in both cases have been suggested.

Keywords. Solar energy conversion; photodecomposition of water; tetrathiomolybdate; photocatalyst.

1. Introduction

Interest in redox catalysts has been stimulated by studies on the direct conversion of solar energy into chemical energy. Among various approaches, photodecomposition of water into dihydrogen (H_2) and dioxygen (O_2) has received much attention. Different artificial model systems (Lehn and Sauvage 1977; Kalyanasundaram *et al* 1978; Brown *et al* 1979; Krasna 1979; Delaive *et al* 1979) often include four components: a photosensitizer, an electron transfer relay, a sacrificial electron donor and an electron transfer catalyst. The transition metal complexes, which normally display multiple valence states and absorb in the visible region, should be capable of storing solar energy and simultaneously act as a photosensitizer as well as an electron transfer catalyst. A preliminary report has already appeared (Bhattacharyya *et al* 1982, 1983) on the photogalvanic generation of dihydrogen using tetrathiomolybdate as photocatalyst. The present paper reports, further extension of the work including the possible mechanism involved, overall efficiency of the process and the confirmation of the identity of the photoproducts including dihydrogen.

2. Experimental

$(NH_4)_2 MoS_4$ was synthesized following the method earlier reported (Kruss 1884) and characterized by analytical and spectroscopic data (Diemann and Mueller 1973). The IR spectra were measured as KBr pellets using a spectrophotometer (Perkin Elmer 597). The UV-visible spectra were measured spectrophotometrically (Pye-Unicam, SP8-400).

The photocatalyst was preserved in the dark and a fresh solution was always used. The photogalvanic cell consisted of two half cells connected by a KCl-agar salt bridge. A saturated solution of $(NH_4)_2 MoS_4$ was used as the photoactive anolyte and a 5 M HCl solution as the dark catholyte. A Pt-foil or a carbon rod (obtained from a flashlight dry cell) was used as the anode. The cathode was a Pt-wire subsequently replaced by platinized Pt and Cu wires. Solutions of different pH were

prepared from reagent grade NH_4Cl and NH_4OH. The H_2 gas generated at the dark cathode was collected in an inverted microburette over the cathode wire to measure the volume, or in an inverted tube fitted with septum for its collection by a gas syringe for gas chromatographic analysis. A gas chromatograph (Shimadzu model GCRIA, (TF), TC detector, temperature 80°C) was used to detect H_2 using Ar as the carrier gas.

The anode compartment was illuminated by a 150 W halogen lamp (Biswas 1977; Marks 1980) and the short circuit current was measured using a digital electrometer (Keithley 616) and the voltage by a digital multimeter (HIL). A magnetic balance (Guoy type) was used to measure the paramagnetic susceptibility generated on irradiation of the $(NH_4)_2 MoS_4$ solution. A 15% (w/v) aqueous solution of $NiCl_2 \cdot 6H_2O$ was used as the calibrant. X-band EPR spectrum was measured using a spectrometer (Varian EPR-4). Diphenyl picryl hydrazyl was used as a calibrant.

3. Results and discussion

The photogalvanic cell responsible for the photodissociation of water can be represented as:

$$anode/(NH_4)_2 MoS_4 \text{ (aq. satd.)}//5 \text{ M HCl/cathode}$$
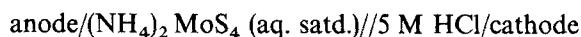
On irradiation of the anode compartment (figure 1) dihydrogen was generated at the cathode and was proved by detecting the gaseous sample by gas chromatography. No H_2 evolution occurred in the dark uptil 10 h after the cell was constructed. The amount of dihydrogen generated per hour depends very much on the anode and cathode materials. The effect of changing the cathode material (table 1) clearly reflects the relative ease of hydrogen evolution on platinized Pt, bright Pt and Cu as determined by the respective overvoltage. Platinized Pt is known to be a better electrocatalyst than bright Pt for this reaction whereas Cu is much inferior. However, the increase in the rate of hydrogen production on replacing a Pt-foil by a carbon rod of approximately the same surface area (*ca* 7·5 cm²) can arise due to two different reasons: (i) difference in the catalytic activities of carbon and Pt for the anode reaction, (ii) the 'real' surface area of carbon may be much greater than the measured 'apparent' surface area due to its somewhat porous nature. The data presented in table 2 illustrate that argument (ii) is a more reasonable explanation. The quantum efficiencies of the hydrogen production (table 1) are not the mono-chromatic values, and hence can be considered as lower limits of actual efficiencies under the given conditions. These values are based on the average number of photons in the visible range received by the anolyte solution which is measured by Reinecke's salt actinometry (Wegner and Adamson 1966). The quantum yield of its photoaquation is assumed to be 0·3 over the entire visible region of the spectrum (Wegner and Adamson 1966).

The measurements of short circuit current with and without illumination provide more quantitative information regarding the mechanism of the overall process. The results are presented in table 2. Since the ratios of the dark and photocurrent densities of Pt and carbon are nearly the same, the effect appears not due to any difference in their catalytic activities. The data in table 2 are based on apparent surface areas. However, a slow rise of the photocurrent (figure 2) to a limiting value seems to indicate a competitive step in the overall reaction mechanism and a consequent slow build-up of electroactive material in the anode compartment.
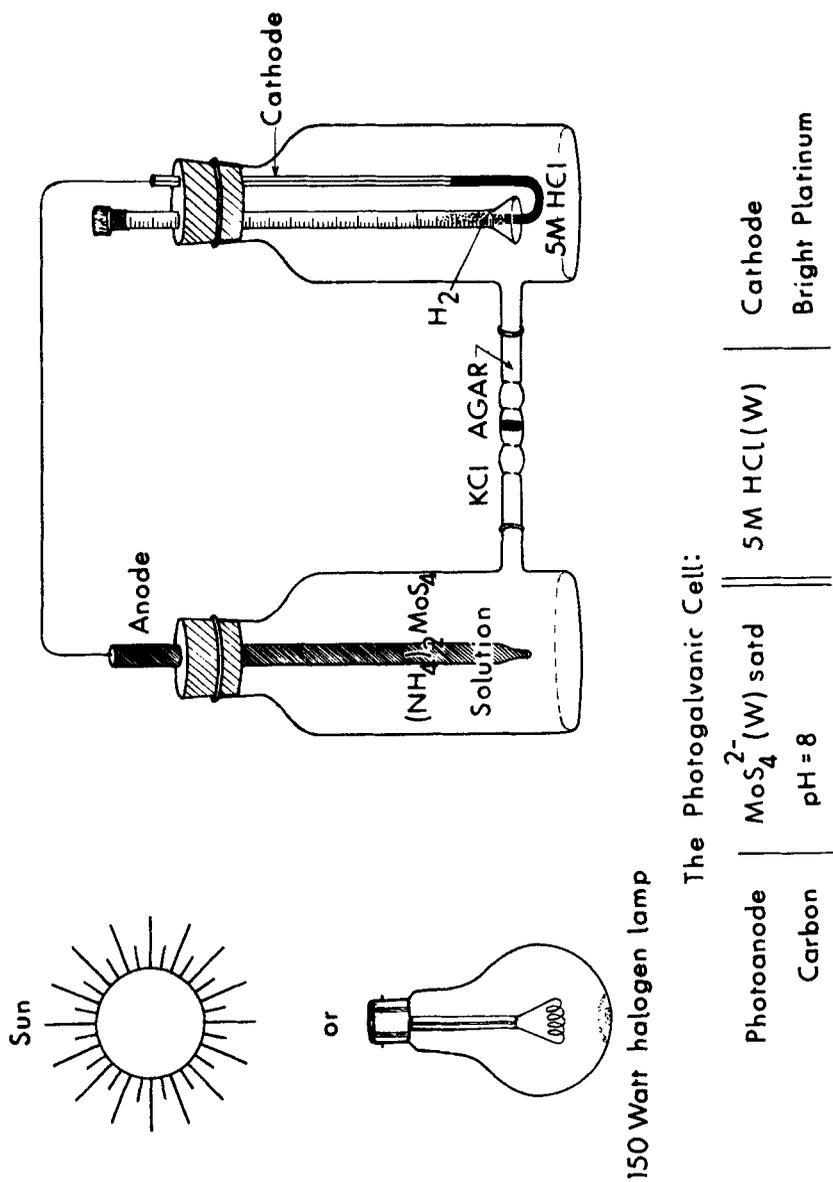
The Photogalvanic Cell:

Photoanode	MoS$_4^{2-}$ (W) satd	5 M HCl (W)	Cathode
Carbon	pH = 8		Bright Platinum

Figure 1. Set-up of the photogalvanic cell.

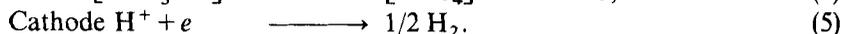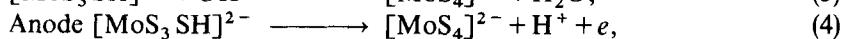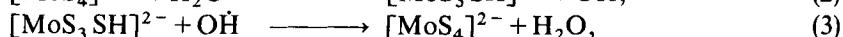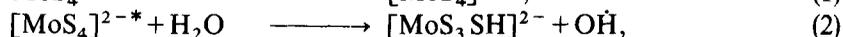**Table 1.** Effect of cathode and anode materials on the rate of photoproduction of dihydrogen.

Anode material	Cathode material	Light intensity (Einstein h^{-1})	Volume of H_2 ($cm^3 h^{-1}$)	Quantum efficiency
Pt-foil	Bright Pt	1.0×10^{-4}	0.03	0.015
	Platinized Pt	1.0×10^{-4}	0.05	0.023
Carbon rod	Bright Pt	5.5×10^{-5}	0.20	0.021
	Platinized Pt	5.5×10^{-5}	0.50	0.038
	Copper	5.5×10^{-5}	Negligible	—

Table 2. Short circuit current density with and without photo-illumination.

| Anode	Short circuit current density (μA cm^{-3})		
	Dark	Light illuminate	Photoeffect
Pt-foil	2.0	12.0	10.0
Carbon rod	16.0	96.0	80.0
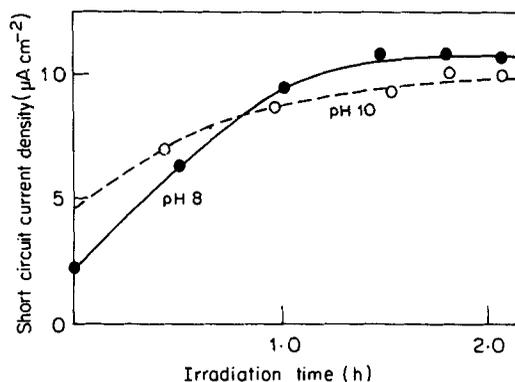
Figure 2. Rise of short circuit current densities with irradiation time in solutions of pH 8.

Based on the above observations the following sequence of steps [equations (1) to (5)] may be suggested for photoproduction of H_2 using MoS_4^{2-} as the photocatalyst. The scheme is similar to the one proposed by Yamase and Ikawa (1979) for heptamolybdate system.

$$MoS_4^{2-} \xrightarrow{\ h\nu\ } [MoS_4]^{2-*}, \tag{1}$$

$$[MoS_4]^{2-*} + H_2O \longrightarrow [MoS_3SH]^{2-} + O\dot{H}, \tag{2}$$

$$[MoS_3SH]^{2-} + O\dot{H} \longrightarrow [MoS_4]^{2-} + H_2O, \tag{3}$$

$$\text{Anode } [MoS_3SH]^{2-} \longrightarrow [MoS_4]^{2-} + H^+ + e, \tag{4}$$

$$\text{Cathode } H^+ + e \longrightarrow 1/2\ H_2. \tag{5}$$

This sequence assumes step (3) to be competitive with the anode reaction. Once a steady state concentration of $[MoS_3SH]^{2-}$, a Mo(V) complex, as against MoS_4^{2-} which contains Mo(VI), is reached, the photocurrent attains a limiting value. The

main water splitting reaction according to the above mechanism can then be represented as:

$$H_2O \longrightarrow 1/2\,H_2 + O\dot{H}.$$
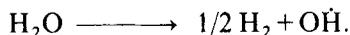
Hydrogen gas evolved identified gas-chromatographically (TC detector, He-carrier). Carbon is known to be a better heterogeneous catalyst than Pt (Ives and Janz 1961) for the combination of $O\dot{H}$ radicals leading to the formation of H_2O_2 which may be decomposed subsequently as follows:

$$2O\dot{H} \longrightarrow H_2O_2 \longrightarrow H_2O + 1/2\,O_2.$$
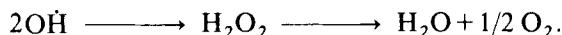
However, O_2 does not evolve from the anode compartment since the H_2O_2 formed immediately reacts with $MoS_4{}^{2-}$ or its hydrolysis or photolysis products forming, among other decomposition products, peroxomolybdates (VI) [evidenced by isolating Ph_4P salt from which $O_2{}^{2-}$ ligand can be detected by IR (ca. $840\,cm^{-1}$)]. The catalyst thus gets deactivated all the time and this explains why a saturated solution of the photocatalyst $(NH_4)_2\,MoS_4$ is necessary to ensure a steady evolution of H_2 and the rise of photocurrent. The catalyst, however, can be easily regenerated (vide infra).

Further evidence in support of the said mechanism (digrammatically represented in figure 3) is obtained by following the change in the magnetic property of an aqueous solution of $(NH_4)_2\,MoS_4$ on irradiation. On exposure to light, the solution develops paramagnetism as expected if Mo(V) species are produced, and reaches a limiting value after 1·5 h (figure 4) ($O\dot{H}$ radicals are too shortlived to get detected). The striking similarity between the rise in photocurrent and the growth of paramagnetism with time provides valid support to our tentative reaction scheme and places it on a firmer basis. The percentage conversion of MoS_4^{2-} (figure 4) has been calculated from the experimental paramagnetic susceptibility measurements of the irradiated solution and the theoretically computed values for $(NH_4)_2\,Mo^V S_3\,SH$
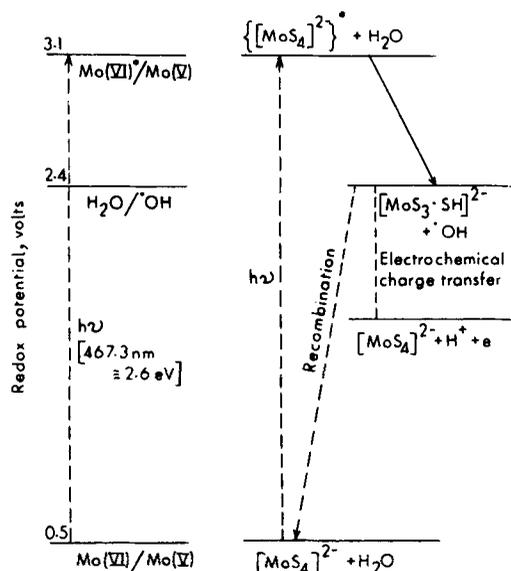

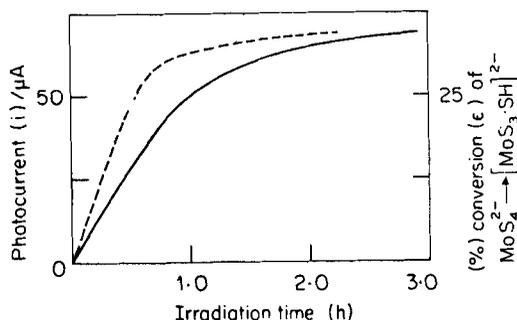**Figure 3.** Energy level scheme of the photo-reaction (energy in volts)

Figure 4. Rise of photocurrent (solid curve) and the growth of paramagnetism (dashed curve) with irradiation time.

considering the 'spin-only' magnetic moment. Furthermore, after 2 h of irradiation the anode solution becomes EPR-active ($g_{av} = 1.98$; featureless) and this also supports our suggested mechanism. The decay curves for photocurrent and paramagnetism obtained after switching off the light source are also identical in pattern. However, while the photogenerated paramagnetism disappears almost completely within 1.5 h or so, a much longer time (even overnight) is needed for the shortcircuit current to return to its initial (dark) value. This is due to a secondary dark reaction which sets in after 10 h of the start of the photoreaction. The dark reaction is initiated by the hydrolysis product of MoS_4^{2-} (i.e. $MoOS_3^{2-}$ and $MoO_2S_2^{2-}$, vide infra) as has been observed by actual experiments. This dark reaction, leading to photodecomposition of water, however, does not involve any monomeric Mo(V) step and that is why the paramagnetism decays out while the photocurrent and H_2 evolution still continues even after switching off the light. It is difficult to arrive at a firm conclusion regarding the mechanism of the dark reaction.

All the above experiments were performed in solutions of pH around 8 as the photocatalyst is only stable in alkaline solution. However, $(NH_4)_2 MoS_4$ undergoes a slow hydrolysis in aqueous solution according to the following reaction (equation (6)) where step-wise replacement of S atoms by O atoms occurs:

$$(NH_4)_2 MoS_4 + nH_2O \longrightarrow (NH_4)_2 MoO_nS_{4-n} + nH_2S \, (n = 1, 2, 3 \text{ or } 4). \quad (6)$$

A part of the generated H_2S may dissolve and dissociate to give HS^- and S^{2-} ions. Although the dissociation constants are very small in the acid solution (1.1×10^{-7} and 1×10^{-4} respectively) these may increase appreciably with increase in pH of the solution. Thus a redox couple H_2S/S^{2-} may exist at a higher pH since cyclooctasulphur (S_8) has a tendency to dissolve in alkaline solution, containing excess of S^{2-} forming polysulphides (S_x^{2-}; $x = 2$–6). The redox potential of the reaction:

$$2H^+ + S + 2e \rightarrow H_2S$$
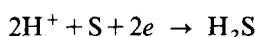
at pH 7 is 0.14 V (Diemann and Mueller 1973). It has been observed that at pH 10 the dark short-circuit current has appreciably higher values leading to some amount of dihydrogen generation even in the dark. This seems possible in view of the negative Nernst potential, calculated for the couple H_2S/S at these higher pH values. However, the photocurrent generation remains essentially of the same nature (figure 1).

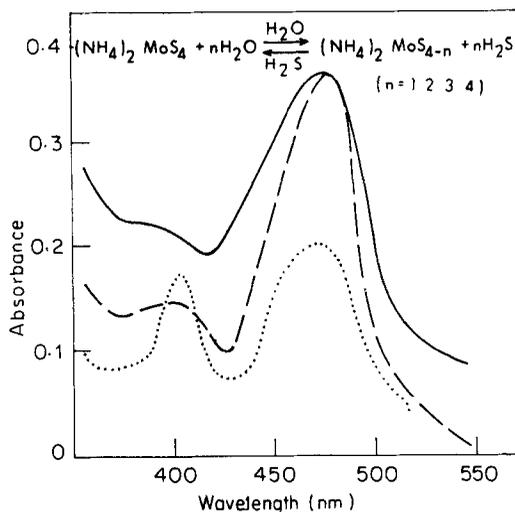**Figure 5.** Electronic spectra of an aqueous solution of $(NH_4)_2 MoS_4$: (———) initial, (. . . . .) 48 h after the photoreaction starts, and (— — —), the regenerated catalyst after passing H_2S.

Due to the slow hydrolysis as shown in equation (6), occasional reactivation by passing H_2S through the anode solution (rendered inactive after 4–5 days) has been found necessary and the effect is obvious from the action spectrum (uv- vis, figure 5) of the solution. By such reactivation, $(NH_4)_2 MoS_4$ catalyst for water photodecomposition can be used for long periods of time.

Acknowledgement

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