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HYDROGEN EVOLUTION FROM WATER WITH VISIBLE RADIATION IN PRESENCE OF Cu(II)/WO_3 AND ELECTRON RELAY

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Abstract—Cu(II)-doped WO_3 particles in presence of methylviologen and visible radiation are found to evolve hydrogen from water more efficiently. Methylviologen has been used as an electron relay for the transfer of conduction band electron of the semiconductor to the hydrogen ion present in the aqueous solution. Increase in the molar percentage of Cu(II) ions is found to increase the hydrogen evolution rate.

NOMENCLATURE

MV^{2+}	Methylviologen dication
$MV^{\cdot +}$	Methylviologen radical cation
e^-_{cb}	Conduction band electron
h^+_{vb}	Valence band hole

INTRODUCTION

The use of sacrificial [1–6] and non-sacrificial [7, 8] agents for the production of hydrogen from aqueous solution by the semiconductor particulate systems is found to be useful and it is also one of the fruitful ways for the conversion of optical energy into chemical energy. Furlong *et al.* [9] have reported hydrogen production with Pt/TiO_2 catalysts using EDTA as the sacrificial agent. Our earlier report [1] on hydrogen production using WO_3 deals with the use of oxalic acid as the sacrificial agent. There are also reports available on the use of sacrificial agents, sulfides [10–13], thiosulfate [14–17], acetic acid [18], EDTA [19], formic acid [20] and alcohols [21] for the production of hydrogen. However, since the quantity of hydrogen generated depends upon the amount of the sacrificial agent used, it is highly desirable to use a non-sacrificial agent for this purpose. Methylviologen (1,1′-dimethyl-4,4′-bipyridium dichloride, MV^{2+}) has been found to be a very good non-sacrificial agent. Reports [7, 8, 22] available with this electron relay indicate that methylviologen could be reduced to methylviologen radical cation by the conduction band electron formed during irradiation of the semiconductor [22] and this radical cation is capable of reducing H^+ to H_2 [23]. Ebbesen [7] has clearly discussed the possibility of generating hydrogen using MV^{2+} through the following schematic equilibrium:

$$MV^{2+} + e^-_{cb} \rightarrow MV^{\cdot +} \quad (1)$$

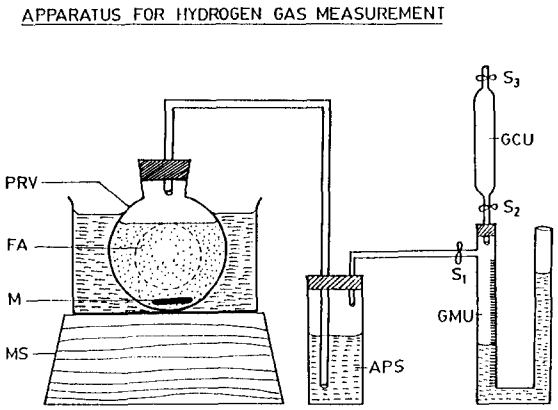
$$2MV^{\cdot +} + 2H^+ \underset{Pt}{\overset{K}{\rightleftharpoons}} 2MV^{2+} + H_2. \quad (2)$$

Considering the energy levels of the conduction bands of various semiconductors, CdS is found to be a good candidate for hydrogen generation, since the conduction band energy level of CdS is more negative than the H^+/H_2 level. However, due to photocorrosion, the potential use of CdS for the production of hydrogen using visible radiation is very much limited. In general, oxide semiconductors are found to be more stable towards photocorrosion than the sulfide semiconductors. Among the oxide semiconductors, many investigations were carried out with TiO_2 [9, 24, 25]; its conduction band energy level is nearer to H^+/H_2 level. However, due to its wide band-gap energy (3.2 eV), it needs light of $\lambda < 400$ nm for the photoexcitation and promotion of electrons from the valence band to the conduction band level. But the band-gap energy of WO_3 is very well suited with the visible region of the solar radiation ($E_g = 2.6$–2.8 eV) and the absorbance of WO_3 in the same wavelength region could also be increased by doping with transition metal ions [26]. However, the conduction band energy level is not negative enough to reduce H^+ to H_2. Hence, an electron relay to mediate the electron-transfer from the conduction band to H^+ is mandatory.

In this article, we report hydrogen production from water using undoped and Cu(II)-doped WO_3 powders by irradiating suspensions of them in the presence of methylviologen with light of wavelength 437 nm. Photosplitting of water into H_2 and O_2 has been observed with Cu(II)-doped sample with high efficiency.

EXPERIMENTAL

Cu(II) doping on WO_3 was done as reported earlier [1]. Methylviologen from Fluka was used as such. Particle sizes [27] of the photocatalysts prepared were in the range 1–10 μ and the surface area determined by BET [27] method was ~ 1.0 m^2 g^{-1}. Methylviologen solution was prepared with doubly distilled water ($[MV^{2+}] = 1.0 \times 10^{-4}$ mol dm^{-3}). In all the experiments, 75 mg of the photocatalyst powders were suspended in 75 ml of MV^{2+} solution (except for catalyst



PRV: Pyrex Reaction Vessel; FA: Flattened Area; M: Stirring Magnet; MS: Magnetic Stirrer; APS: Alkaline Pyrogallol Solution; GMU: Gas-Measuring Unit; GCU: Gas Collecting Unit; S_1, S_2, S_3: Stoppers

Fig. 1. Apparatus for hydrogen gas measurement.

amount variation). The light source used was a high pressure Hg-lamp (250 W, Applied Photophysics, London). After filtering the IR and UV radiations by a water jacket and a glass filter respectively, the emitted radiation corresponds to λ = 437 nm only. The volume of hydrogen evolved was measured using the apparatus which is schematically shown in Fig. 1. A round bottom flask (pyrex) was used as the reaction vessel. The front portion of the flask was flattened through which light was focused into the vessel. The reaction medium and the whole apparatus were flushed with argon before the reaction was started. The gaseous products formed during irradiation were passed through Fieser's solution to remove the oxygen formed and then allowed to enter into the gas measuring tube. At first, the stopper (1) was opened and the stoppers (2) and (3) were closed. The gas was collected in the gas measuring tube slowly by displacing the water due to the pressure developed inside the reaction vessel. Since the gas collecting tube was graduated, the amounts of gas collected at different time intervals were noted. After the evolution of a considerable amount of gas, stopper (1) was closed and stopper (2) was slowly opened and the gas was collected in the gas collecting unit. The process was repeated until a considerable amount of gas was collected in the gas collecting unit for GC analysis.

RESULTS AND DISCUSSION

Photocatalytic experiments carried out with Cu(II)-loaded WO_3 powders in the presence of MV^{2+} solution were efficient in hydrogen production. The undoped WO_3 powders in presence of MV^{2+} exhibited very poor performance in hydrogen production. Blank experiments were also carried out (1) without catalyst powder in the presence of light and MV^{2+}, (2) without MV^{2+} in the presence of light and catalyst powder and (3) without light in the presence of MV^{2+} and catalyst powder. No hydrogen production was observed in any case which confirms that the evolution of hydrogen could be achieved only by the illuminated photocatalyst particles in aqueous solution of MV^{2+}.

Figure 2 shows the plots of the amount of hydrogen produced with time by Cu(II)-doped WO_3 powders for 1.0 to 5.0 molar percentages of Cu(II)-ions. In general, it is found that the amount of hydrogen evolved increases with increase in time and with increase in the percentages of Cu(II)-ions. Undoped WO_3 shows very poor efficiency. It is a known fact that the energy level of the conduction band of WO_3 is not negative enough to reduce H^+ to H_2. However, it is capable of reducing MV^{2+} to $MV^{\cdot+}$ efficiently in the presence of the dopant. As reported earlier [1], Cu(II) traps the conduction band electron and efficiently transfers it to methylviologen dication which is then reduced to radical cation. This radical cation is capable of reducing H^+ to H_2. The formation of $MV^{\cdot+}$ from MV^{2+} by photoin-

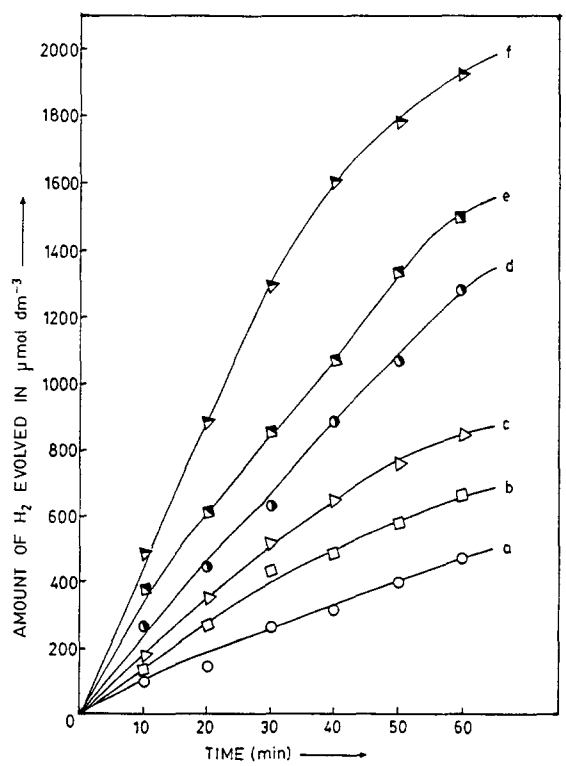


Fig. 2. Amount of H_2 evolved vs time: (a) Undoped WO_3; (b) 1.0% Cu(II)/WO_3; (c) 2.0% Cu(II)/WO_3; (d) 3.0% Cu(II)/WO_3; (e) 4.0% Cu(II)/WO; (f) 5.0% Cu(II)/WO_3.

duced electron-transfer in the presence of a semiconductor [28], reduction of H^+ by $MV^{\cdot +}$ [23] and the catalysis of this process by metals [29] are already available in literature. Simultaneous evolution of oxygen from water is also observed since the valence band level of WO_3 is well below the water oxidation level [30]. Based on the above discussion, the following reaction mechanism is proposed:

$$WO_3 \xrightarrow[\lambda = 437\ \text{nm}]{h\nu} h^+_{vb} + e^-_{cb} \quad (2)$$

$$Cu(II) + e^-_{cb} \rightarrow Cu(I) \quad (3)$$

$$Cu(I) + MV^{2+} \rightarrow Cu(II) + MV^{\cdot +} \quad (4)$$

$$h^+_{vb} + H_2O \rightarrow OH + H^+ \quad (5)$$

$$MV^{\cdot +} + H^+ \rightarrow MV^{2+} + \tfrac{1}{2} H_2 \quad (6)$$

$$2\dot{O}H \rightarrow H_2O_2 \rightarrow \tfrac{1}{2} O_2 + H_2O. \quad (7)$$

The reactions (2) and (3) are taking place inside the WO_3 lattice whereas the reactions (4)–(6) are at the particle–electrolyte interface. The hydrogen evolved was identified by gas chromatography and oxygen evolution was confirmed using an oxygen sensitive electrode. It is known that $MV^{\cdot +}$ radicals are unstable to O_2 [23]. From the fact that O_2 and H_2 are simultaneously produced in the reactions, it may be pointed out that in presence of Cu(II)-doped WO_3 particles, the reduction of H^+ to H_2 is enhanced over that of the reaction between $MV^{\cdot +}$ and O_2. Although in the absence of any other additive, $MV^{\cdot +}$ is long lived, as its disproportionation is an endoergic reaction, in the presence of the dopants it is capable of reducing water itself to hydrogen and hydroxide ions [31]. The above explanation could be supported by the fact that the undoped WO_3 particles showed very poor efficiency and with increased molar percentage of the dopant, the efficiency is enhanced. As the percentage of Cu(II) ions is increased, more and more conduction band electrons are trapped and utilized for hydrogen production. In other words, the electron–hole recombination process is reduced by the increased dopant concentration. Cu(II) ions are introduced into the WO_3 lattices during sintering which has been proved by the diffuse reflection study [26]. These dopant ions introduce "isolated energy levels" inside the band-gap of the host molecules and help to increase the absorbance of WO_3 particles in the visible region of the solar radiation [26]. These dopant ions are also present on the surface of WO_3 particles, as observed from SEM [27] pictures, which act as electron–transfering agents and catalyse the reactions (3) and (4).

Photocatalytic experiments were also carried out with

Table 1. Variation of the catalyst amount

Catalyst amount, mg	Amount of H_2 evolved in 60 min, mM
25	0.926
50	1.528
75	1.917
100	1.872
125	1.880

Catalyst = 5.0% Cu(II)/WO_3; $[MV^{2+}] = 1.30 \times 10^{-4}$ mol dm^{-3}.

Table 2. Variation of $[MV^{2+}]$

$[MV^{2+}] \times 10^4$, mol dm^{-3}	Amount of H_2 evolved in 60 min, mM
0.27	1.821
0.53	1.912
0.80	1.877
1.30	1.917

Catalyst = 5.0% Cu(II)/WO_3; Catalyst amount = 75 mg.

various amounts of catalyst powders keeping constant [dopant] (5.0 molar percentage) and $[MV^{2+}]$ (1.3×10^{-4} mol dm^{-3}) and the results are presented in the Table 1. With an increase in catalyst amount, the amount of hydrogen produced increased up to a certain limit and remained almost constant beyond that level. A maximum is reached with 75 mg of the catalyst powder. This observation is a well known phenomenon in heterogeneous catalysis, namely Langmuir adsorption kinetics, which has been explained earlier [32]. Experiments carried out with various initial concentrations of MV^{2+} (Table 2) showed that $[MV^{2+}]$ does not influence the hydrogen evolution rate.

CONCLUSION

Along with noble metal ions [8, 29], Cu(II) could also be used as a dopant which is capable of catalysing the reaction $MV^{2+}/MV^{\cdot+}$ for the reduction of H^+ to H_2.

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REFERENCES

1. P. Maruthamuthu and M. Ashokkumar, *Int. J. Hydrogen Energy* **13**, 677 (1988).
2. A. Ueno, N. Kakuta, K. H. Park, M. F. Finlayson, A. J. Bard, A. Campion, M. A. Fox, S. E. Webber and J. M. White, *J. Phys. Chem.* **89**, 3828 (1985).
3. N. Kakuta, K. H. Park, M. F. Finlayson, A. Ueno, A. J. Bard, A. Campion, M. A. Fox, S. E. Webber and J. M. White, *J. Phys. Chem.* **89**, 732 (1985).
4. K. Hashimoto, T. Kawa and T. Sakata, *J. Phys. Chem.* **88**, 4083 (1984).
5. J. Kobayashi, K. Kitaguchi, H. Tanaka, H. Tsuiki and A. Ueno, *J. Chem. Soc. Faraday Trans. 1*, **83**, 1395 (1987).
6. R. Rafaeloff, Y.-M. Tricot, F. Nome and J. H. Fendler, *J. Phys. Chem.* **89**, 533 (1985).
7. T. W. Ebbesen, *J. Phys. Chem.* **88**, 4131 (1984).
8. P. Maruthamuthu and M. Ashokkumar, *Proc. Seventh Int. Conf. Photochemical Conversion and Storage of Solar Energy*, Northwestern University, Illinois, p. 109 (1988).
9. D. N. Furlong, D. Wells and W. H. F. Sasse, *J. Phys. Chem.* **89**, 626 (1985).
10. M. Butler, K. Meier and J-F. Reber, *J. Phys. Chem.* **88**, 3261 (1984).
11. A. B. Ellis, S. W. Kaiser and M. S. Wrighton, *J. Am. Chem. Soc.* **98**, 6855 (1976).
12. H. Minoura and M. Tsuiki, *Electrochimica Acta* **23**, 1377 (1978)
13. T. Inove, J. Watanabe, A. Fujishima and K. Honda, *Bull. Chem. Soc. Jpn* **52**, 1243 (1979).
14. A. A. Krasnovsky, G. P. Brin and V. V. Mikandrow, *Dokl. Akad. Nauk. SSSR*, **200**, 1214 (1975).
15. S. M. Frank and A. J. Bard, *J. Phys. Chem.* **81**, 1484 (1977).
16. B. Kracutler, and A. J. Bard, *J. Am. Chem. Soc.* **100**, 5985 (1978).
17. J. P. Wilson and S. M. Park, *J. Electrochem. Soc.* **129**, 149 (1982).
18. T. Sakata, In E. Pelizetti and N. Serpone (eds), *Homogeneous and Heterogeneous Photocatalysis*, p. 397, Reidel, Dordrecht, The Netherlands (1986).
19. J. P. Harbour, R. Wolkow and M. L. Hair, *J. Phys. Chem.* **85**, 4026 (1987).
20. I. Willner and Z. Goren, *J. Chem. Soc. Chem. Commun.* 172 (1986).
21. a. P. Pichat, M. N. Mozzanega, J. Desdier and J. M. Hermann, *Nouveau J. Chim.* **6**, 559 (1982).
    b. L. T. Prahov, J. Desdier, J. M. Herrmann and P. Pichat, *Int. J. Hydrogen Energy* **9**, 397 (1984).
22. H-C. Youn, Y-M. Tricot and J. H. Fendler, *J. Phys. Chem.* **91**, 581 (1987).
23. M. S. Wrighton, In J. S. Miller (ed), *Chemically Modified Surfaces in Catalysis and Electrocatalysis*, p. 99, ACS, Symposium Series No. 192 (1982).
24. Y. Inone, M. Okamura and K. Sato, *J. Phys. Chem.* **89**, 5184 (1985).
25. R. Baba, S. Makabayashi, A. Fujishima and K. Honda, *J. Phys. Chem.* **89**, 1902 (1985).
26. P. Maruthamuthu and M. Ashokkumar, *Solar Energy Mater.* **17**, 433 (1988).
27. M. Ashokkumar and P. Maruthamuthu, *J. Mater. Sci.* 1989 (in press).
28. Y. Nosaka, H. Miyama, M. Terauchi and T. Kobayashi, *J. Phys. Chem.* **92**, 255 (1988).
29. J. M. Lehn, J. P. Sauvage and R. Ziessel, *Nouveau J. Chim.* **4**, 623 (1980).
30. W. Erbs, J. Desilnestro, E. Borgarello and M. Gratzel, *J. Phys. Chem.* **88**, 4001 (1984).
31. a. D. Duonghong, E. Borgarello and M. Gratzel, *J. Am. Chem. Soc.* **103**, 4685 (1981).
    b. D. Duonghong, J. Ramsden and M. Gratzel, *J. Am. Chem. Soc.* **104**, 2977 (1982).
32. P. Maruthamuthu, M. Ashokkumar and L. Venkatasubramanian, *Bull. Chem. Soc. Jpn* **61**, 4137 (1988).