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Photobiocatalytic production of hydrogen using sensitized TiO_2–MV^{2+} system coupled *Rhodopseudomonas capsulata*

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Abstract

Intact cells of *Rhodopseudomonas capsulata*, as photocatalyst for hydrogen production using light of $\lambda > 400$ nm, were added to a slurry of naked or sensitized TiO_2 semiconductor containing MV^{2+} as an electron relay. It is discussed that the nitrogenase enzyme of the bacterial cells is responsible for catalyzing hydrogen production. Sensitization of TiO_2 was performed in three ways: (1) using organic dyes, (2) using Cu(II) ion doping, (3) loading with low-band gap semiconductors (CdS). In the four components, i.e., TiO_2/MV^{2+}/electron donor/bacterial cells, each of the last three components has its own specific function and each facilitates the others' role, thereby enhancing the yield of hydrogen production. It was found that with sensitized TiO_2, there is a higher amount of hydrogen production than with the naked TiO_2. Among the sensitizers used, Rhodamine B and $Ru(bpy)_3^{2+}$ exhibited higher efficiencies compared with other sensitizers, as well as other method of sensitization (2 and 3). The effects of electron donors, divalent metal ions (Mn^{2+}, Mg^{2+} and Ca^{2+}) to the above system were also studied. Suitable mechanisms and schematic models are proposed, in accordance with the observations, for the different kinds of catalytic systems employed in the present study.

Keywords: Photobiocatalytic production; Hydrogen; Sensitized TiO_2–MV^{2+} system; *Rhodopseudomonas capsulata*

1. Introduction

Hydrogen can be generated from water photocatalytically, photobiologically, and photoelectrochemically. Photobiocatalytic method is a novel method of hydrogen production by coupling inorganic semiconductor with bacterial enzyme. We have reported on photocatalytic hydrogen production with $Cu(II)/WO_3$ [1,2], $Cu(II)/Bi_2O_3$ [3], $Rh(III)/Fe_2O_3$ [4], Pt/SnO_2 [5] using methyl viologen. We have reported photobiocatalytic hydrogen production using undoped/doped Bi_2O_3 coupled with photosynthetic bacteria [6].

Since oxide semiconductors generally have a wide band gap, they absorb only very little part of light in the visible region and this drawback could be overcome by sensitization. We have already reported about the use of the first type of sensitization for WO_3 [7]. Dobestani et al. [8] have achieved sensitization of TiO_2 and $SrTiO_3$ electrodes by using the photosensitizers Ruthenium (II) tris(2,2′-bipyridine-4,4′-dicarboxylic acid) and Zinc tetrakis(4-carboxyphenyl por-

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phyrin). They also sensitized TiO_2 by CdS-loading and this effect was ascribed to more efficient charge separation caused by an inter-particle electron transfer from the excited CdS either to the conduction band of TiO_2 or directly to the redox catalyst [9]. The CdS/TiO_2 system exemplifies the third type of sensitization.

Another requirement for the photoproduction of hydrogen using a semiconductor is the need for a hydrogen evolution catalyst on semiconductor surface as reported by many research groups [10]. We have also investigated the role of Pt, Pd and Rh on WO_3 for the photocatalytic production of hydrogen from aqueous methyl viologen [11]. Similar to metal, metal oxide, e.g., RuO_2 can also serve as the catalyst for hydrogen production [12]. But a better catalyst has the origin in biology, i.e, bacterial enzyme which catalyses the hydrogen evolution [13]. Nikandrov et al. [14] coupled bacterial enzyme from *Thiocapsa roseopersina* to TiO_2 and observed an efficient photobiocatalytic hydrogen production.

In the present study, TiO_2 was sensitized individually in all three ways and coupled to intact bacterial cells of *Rhodopseudomonas capsulata* species. The semiconductor-bacterial cells system is then subjected to hydrogen in aqueous solution under visible light using MV^{2+} as an electron relay with or without electron donor.

2. Experimental

2.1. Materials

CdS (semiconductor grade 99.99%) was from Koch-Light Laboratories, England. Semiconductor grade TiO_2 (99.999%) and methyl viologen (1,1′-dimethyl-4,4′-bipyridinium dichloride) were from Aldrich, USA. $Ru(bpy)_3Cl_2$ was prepared by standard procedure [15]. Rose Bengal, Eosine Blue and other chemicals used were of research grade.

2.2. Strain and cultivation

R. capsulata strain 11166 was a kind gift from Dr. T.M. Vathsala, Deputy Director, Sri A.M.M. Murugappa Chettiar Research Centre, Madras, India. This bacteria is photosynthetic and has both nitrogenase and hydrogenase enzymes. For our studies, a hydrogen evolving enzyme (nitrogenase) is present in the above bacteria and it exhibited the fastest growth rates under photoautotrophic conditions. The bacterial cells were grown under standard photosynthetic conditions [16].

2.3. Sensitization of TiO_2

TiO_2 was sensitized in three ways. It was doped with Cu(II) ion (4 at.%) using the method of Dimetrijevic et al. [17]. Another portion of the TiO_2 was loaded with CdS powder (10% *w/w*) by mechanical mixing and sintering at 300°C under argon atmosphere for 8 h. Naked TiO_2 was employed along with inorganic $Ru(bpy)_3^{2+}$ or organic dyes as photosensitizers.

2.4. Characterization of materials

The prepared photocatalysts were characterized by diffuse absorption spectra (Cary 2300 Model) using $BaSO_4$ as the reference and the difference absorption spectra of the doped TiO_2 were drawn from the difference in absorption of undoped and doped TiO_2.

2.5. Procedure

In all the experiments, 80 mg of the photocatalyst dispersed in 80 ml of the solution containing 50 μM of MV^{2+}, 4 ml of intact bacterial cells (the estimated bacterial weight in above volume solution is 2.4 mg/dry weight), and 0.01–0.1 mol/dm^3 of electron donor (Tris–HCl, glycerol, oxalic acid and EDTA) taken in a Pyrex glass photoreactor and thermostated at 25°C was irradiated with 150 W Xenon arc lamp (Applied Photophysics, London). The light

was filtered through 380 nm filter and passed through a water jacket (to remove IR light) before falling on the photoreactor. The light intensity was measured by potassium ferrioxalate actinometry method [18] and was found to be 0.51×10^{-8} einsteins/cm^2/s. The reaction medium and the whole apparatus was flushed with argon for 30 min before irradiation. The evolved gas passed through 50% KOH solution to absorb CO_2 (if formed due to the presence of electron donor) and alkaline pyrogallol solution at 0–5°C to remove oxygen (if formed due to water oxidation by valence band holes) and the rest of the gas was collected in a water manometer. The collected gas was detected as hydrogen by GC (Chromatography and Instruments, India) using molecular sieves 5 Å column and argon as the carrier gas.

2.6. Quantum yield

As reported earlier [4], quantum yields for photobiocatalytic hydrogen production using undoped/doped TiO_2 semiconductor coupled with photosynthetic bacteria were calculated by the formula,

$$\text{Quantum yield}\,(\phi) = \frac{2 \times \text{H}_2 \text{ rate (M/s)}}{\text{Photon rate (Einstein/s)}}. \quad (1)$$

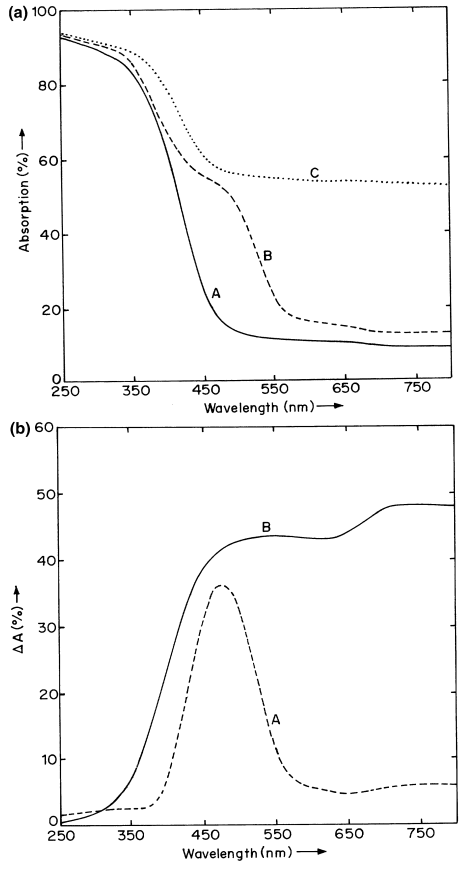


Fig. 1. (a) Diffuse absorption spectra of (A) undoped TiO_2, (B) 10% *w*/*w* CdS/TiO_2, (C) 4 at.% Cu(II)/TiO_2. (b) Difference absorption spectra of (A) 10% *w*/*w* CdS/TiO_2, (B) 4 at.% Cu(II)/TiO_2.

3. Results and discussion

3.1. Characterization

In order to get an information about the extent of the absorption of the undoped and doped TiO_2 in the visible region, the photocatalysts were characterized by diffuse absorption spectra. Fig. 1a,b are the diffuse absorption and difference absorption spectra respectively of undoped and doped TiO_2. Fig. 1a shows that TiO_2 has only 65% absorption at 400 nm, whereas Cu(II)/TiO_2 has about 80% absorption extended to about 650 or 700 nm in visible region and for CdS/TiO_2 has around 65% absorption at 400 nm and another strong absorption at 500 nm due to CdS loading. Thus, the extent, as well as the range of absorption of undoped TiO_2 is greatly enhanced by the doping or loading process, due to the phenomenon called ''sensitization of semiconductor'' [17]. From Fig. 1b, we inferred that the difference in absorption is only due to Cu(II) doping and CdS loading.

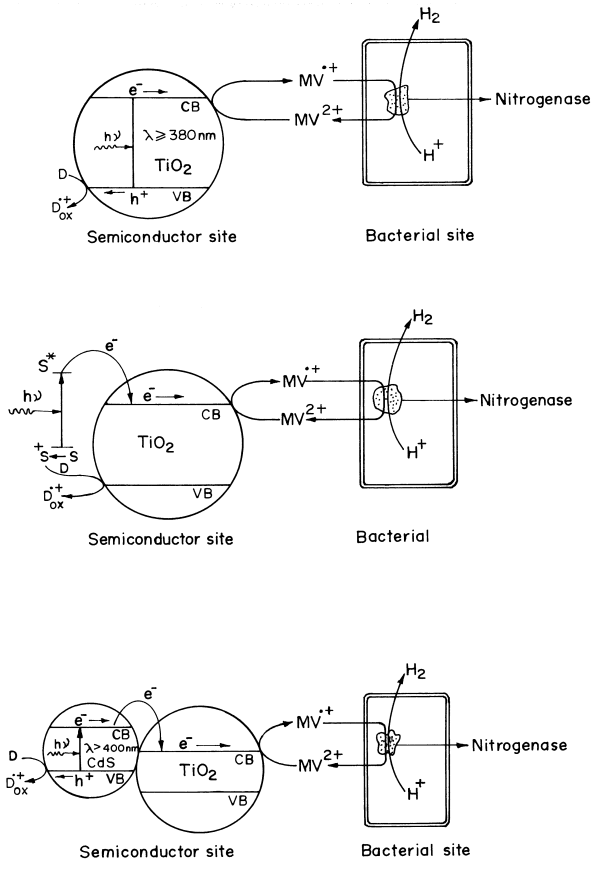
3.2. Hydrogen production naked TiO_2/MV^{2+}/Tris–HCl/R. capsulata system

Hydrogen production from an aqueous suspension containing TiO_2, Tris–HCl buffer (pH

Table 1
Photobiocatalytic hydrogen production with naked TiO_2/MV^{2+}/Tris–HCl/*R. Capsulata* system
$[MV^{2+}] = 5 \times 10^{-5}$ mol/dm^3; [Tris–HCl] = 0.05 mol/dm^3; pH = 7.2; bacterial cells = 4 ml.

System	Volume of H_2 evolved (ml/h)	Quantum yield
TiO_2 + Tris–HCl	0.0	0.0
TiO_2 + Tris–HCl + *R. capsulata*	0.3	2.3
TiO_2/MV^{2+}/Tris–HCl	0.2	1.5
MV^{2+}/Tris–HCl/*R. capsulata*	0.2	1.5
TiO_2/MV^{2+}/*R. capsulata*	0.4	3.0
TiO_2/MV^{2+}/Tris–HCl/*R. capsulata*	0.7	5.2
Dithionite/MV^{2+}/Tris–HCl/*R. capsulata* (dark reaction)	0.6	–

= 7.2) as an electron donor, MV^{2+} as an electron relay, and bacterial enzyme as hydrogen evolution catalyst was investigated and results are tabulated in Table 1. It was found that hydrogen is not evolved in the absence of both electron relay and bacterial cells and it was observed that there is no direct electron transfer between semiconductor and bacterial enzyme. However, little amount of hydrogen was evolved when anyone of them is coupled with semicon-



Scheme 1. Photobiocatalytic hydrogen production using TiO_2 semiconductor coupled to bacterial nitrogenase.

Scheme 2. Photobiocatalytic hydrogen production using photosensitizer sensitized TiO_2 semiconductor coupled to bacterial nitrogenase.

Scheme 3. Photobiocatalytic hydrogen production using CdS/TiO_2 semiconductor coupled to bacterial nitrogenase.

ductor/Tris–HCl. When all the four components are present, the rate of hydrogen production is found to be relatively high than the system containing the absence of anyone of the above four components. From Table 1, it is clear that the role of MV^{2+} as an electron relay is more important than the role of bacterial enzymes and if both are present, each facilitates the others' role.

Enzyme catalyst is more specific for hydrogen evolution than Pt, because the latter catalyses the hydrogenation of MV^{2+} in addition to hydrogen evolution [18]. In system containing intact bacterial cells, their coupling to photocatalyst particles may proceed via reduced methyl viologen capable of cell membrane penetration (Scheme 1)

Hydrogen production by a dark reaction was also possible when MV^{2+} was reduced with dithionite [14]. The rate of hydrogen production in the dark reaction is comparable with the rate of photoinduced hydrogen production for which the quantum yield is 5.2.

3.3. Hydrogen production with sensitized TiO_2/MV^{2+}/Tris–HCl/R. capsulata system

TiO_2 was sensitized with inorganic $Ru(bpy)_3^{2+}$ and organic (dyes) sensitizers, and used in photobiocatalytic production of hydrogen from aqueous solution containing MV^{2+}, bacterial cells, and electron donor (Tris–HCl buffer). Table 2 presents the effect of various sensitizers on hydrogen production efficiency. The amount of hydrogen produced with sensitized TiO_2 is higher than that of naked TiO_2. This is because of the following possible mechanisms:

- direct electron transfer to the conduction band of the semiconductor from the excited state of the dye/complex molecules;
- energy transfer from the excited state of the dye/complex to the surface state of the semiconductor followed by the electron (or hole) injection from the excited surface states; and
- electron transfer from the excited dye to the surface states and from the surface states to the continuum of the semiconductor.

Among the different sensitizers used, Rhodamine B is found to sensitize the semiconductor to the maximum extent as evidenced from the amount of hydrogen produced (1.6 ml/h). The efficiency of the different sensitizers in the increasing order is as follows:

$$\text{Eosine Blue} < \text{Rose Bengal} < Ru(bpy)_3^{2+} < \text{Rhodamine B}$$

This observed trend may be due to the properties such as redox potentials and λ_{max} of the sensitizers, etc. The first electron reduction potential of the dyes are more negative than the redox potential of MV^{2+}/MV^{+} and the dye injects the electron from the excited state of the

Table 2
Photobiocatalytic hydrogen production using photosensitizer sensitized TiO_2/MV^{2+}/Tris–HCl/*R. capsulata*
$[MV^{2+}] = 5 \times 10^{-5}$ mol/dm^3; $[Ru(bpy)_3^{2+}] = 4 \times 10^{-5}$ mol/dm^3; [Tris–HCl] = 0.05 mol/dm^3; [EB] = 3.75×10^{-5} mol/dm^3; pH = 7.2; [RhB] = 2.5×10^{-5} mol/dm^3; *R. capsulata* = 4 ml; [RB] = 2.5×10^{-5} mol/dm^3. EB = Eosine blue, RhB = Rhodamine B, RB = Rose bengal, S = Photosensitizer.

System	Amount of H_2 evolved (ml/h)	Quantum yield	First e-reduction. potential of S (V vs. SCE)	λ_{max} of S (nm)
TiO_2/MV^{2+}/Tris–HCl/*R. capsulata*	0.7	5.2	–	–
TiO_2/MV^{2+}/Tris–HCl/*R. capsulata* + Ru $(bpy)_3^{2+}$	1.5	11.3	−0.860	454
TiO_2/MV^{2+}/Tris–HCl/*R. capsulata* + EB	1.0	7.5	−0.580	515–518
TiO_2/MV^{2+}/Tris–HCl/*R. capsulata* + RhB	1.6	12.0	−0.545	551–553
TiO_2/MV^{2+}/Tris–HCl/*R. capsulata* + RB	1.1	8.3	−0.533	550

dye to the conduction band of the TiO_2 and easily reduces MV^{2+}/MV^{+}. The combined effect of all these properties of Rhodamine B might be well suited with the properties of TiO_2 (like CB level, surface states) and the light source and so the efficiency of energy transfer might be more effective in Rhodamine B.

The Scheme 2 is proposed to explain the role of bacterial cells, the process of dye sensitization and the electron relay activitiy of MV^{2+}. During illumination, the sensitizer gets excited and injects an electron to the conduction band of TiO_2. This electron, after being carried through the band, is utilized for the reduction of MV^{2+} that is absorbed on the surface of the semiconductor. MV^{+} formed on reduction penetrates through the cell membrane of the intact *Rhodoseudomonas* cell coupled to the semiconductor and reduces H^{+} to H at the bacterial nitrogenase enzyme site that favors the evolution of molecular hydrogen. Such a model has already been proposed [14] for the photobiocatalytic production of hydrogen. It is suggested that the nitrogenase activity is responsible for evolution of hydrogen in the photobiological production of hydrogen [13,19,20]. In general, two classes of enzymes, hydrogenase (iron sulfur protein) and nitrogenase (protein complexes containing iron sulfur and molybdenum), are closely associated with the final hydrogen evolving actively in photosynthetic bacteria. Even though the primary function of the enzymes are quite different (nitrogenase function in biological nitrogen fixation and hydrogenase catalyses hydrogen uptake or consuming reaction) under certain conditions in both catalyse hydrogen production, evolution of hydrogen in photsynthetic bacteria is now known to be a function of nitrogenase rather than hydrogenase [13]. In the absence of nitrogen or NH_4^{+}, nitrogenase enhances the reduction of H^{+} to H_2, whereas the main function of hydrogenase is to catalyse hydrogen uptake reactions. And it is also proved that in the case of *R. capsulata*, mutants defective in nitrogenase activity do not evolve hydrogen [13,21].

3.4. Hydrogen production with 4 at.% Cu(II) / TiO_2 / MV^{2+} / electron donor / R. capsulata

Various electron donors (Tris–HCl, oxalic acid, EDTA and glycerol) were attempted for photobiocatalytic hydrogen production with $Cu(II)/TiO_2$. Under similar conditions, i.e., with Tris–HCl buffer, MV^{2+} bacterial cells, $Cu(II)TiO_2$ produced a higher amount of hydrogen (49.06 $\mu M/h$) than the naked TiO_2 (31.22 $\mu M/h$). This is explicable on the basis of our earlier result [2]. Cu(II) ion is an efficient electron-trapping agent which traps the photogenerated e^{-}_{CB} and efficiently transfers it to MV^{2+}, thereby preventing the e^{-}–h^{+} recombination, a serious handicap in the semiconductor photochemistry. MV^{+} then relays the e^{-} to H^{+} and favors hydrogen production in the presence of the appropriate catalyst. The following reaction mechanism is proposed in accordance with the observation.

$$TiO_2 \xrightarrow{h\nu} h^{+}_{VB} + e^{-}_{CB} \quad (2)$$

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

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

$$MV^{+} + H^{+} \xrightarrow{\text{nitrogenase}} MV^{2+} + 1/2\,H_2 \quad (5)$$

$$h^{+}_{VB} + e^{-}\ \text{donor} \rightarrow \text{oxidized products} \quad (6)$$

Fig. 2 shows the profiles of the rates of hydrogen production with $Cu(II)/TiO_2$ in the

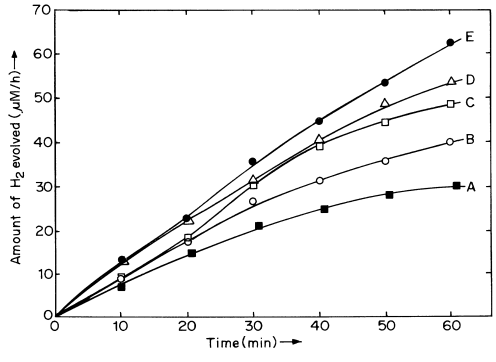


Fig. 2. Photobiocatalytic hydrogen production using various electron donors. System: 4 at.% $Cu(II)/TiO_2$ / *R. capsulata*. (A) without electron donor, (B) glycerol (1 M), (C) Tris–HCl (7.2), (D) EDTA (0.02 M), (E) oxalic acid (0.02 M).

presence of different electron donors. Without an electron donor, there is only a small amount of hydrogen production (22.3 μM/h). But with an electron donor, there is considerably a larger amount, the values being 49.06, 62.40, 53.5, and 40.14 μM/h for Tris–HCl, oxalic acid, EDTA, and glycerol, respectively. The highest value of oxalic acid may be due to its easy oxidation to CO_2, and to the ready uptake of CO_2 by the bacterial cells of photosynthesis, an indirect facilitation for oxalic acid oxidation.

3.4.1. Effect of [oxalic acid] on photobiocatalytic production of hydrogen

As a representation electron donor, the effect of [oxalic acid] is up to 0.04 mol/dm^3 and above that it declines (Fig. 3). This is attributed to the fact that a higher concentration of electron donor may block the active sites of the semiconductor, leading to a less amount of photon absorption, and hence, a decreased photocatalytic efficiency. Similar type of concentration effects have already been observed and reported in our earlier articles [1]. One advantage of this type of study is to know the optimal concentration (in the present case 0.04 mol/dm^3) for maximum yield. There is no greater change in the pH due to low concentration of oxalic acid and it is not toxic to the bugs.

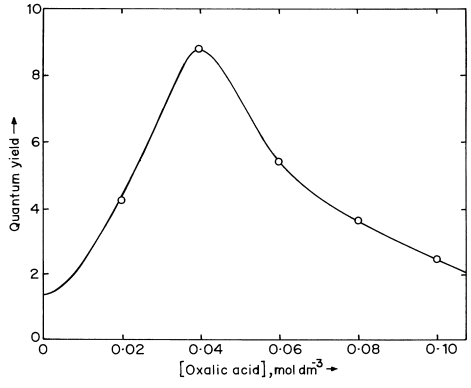


Fig. 3. [Oxalic acid] variation on photobiocatalytic hydrogen production using 4 at.% Cu(II)/TiO_2 / *R. capsulata*.

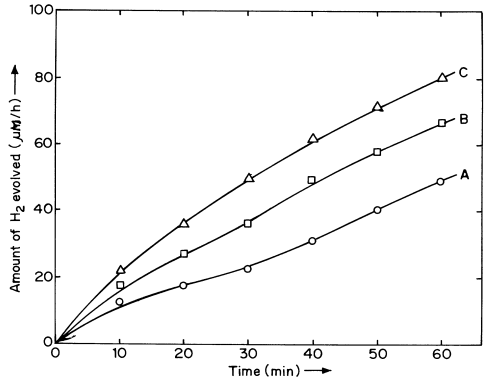


Fig. 4. The effect of metal ions adding on photobiocatalytic hydrogen production using 4 at.% Cu(II)/TiO_2 / *R. capsulata*. [EDTA] = 0.02M. (A) Ca^{2+} (1 mM), (B) Mg^{2+} (1 mM), (C) Mn^{2+} (1 mM).

3.4.2. Effect of metal ions on hydrogen production

Usually, proteins have the tendency to bind metal ions and this binding may change the properties of proteins. Since the bacterial cells are made of proteineous parts, metal ion binding to these cells is likely to affect the catalytic activitiy of the bacterial enzyme contained in the cells. Hence, a study was made with a view to investigate the effect of divalent metal ions (Mg^{2+}, Mn^{2+} and Ca^{2+}) on hydrogen production with the system Cu(II)/TiO_2/MV^{2+}/EDTA/*R. capsulata*. The metal ion may bind as such or in the form of EDTA complex. Anyhow, the catalytic activity of the enzyme is enhanced and the inclusion of metal ions shows an upward trend in the amount of hydrogen production (Fig. 4), the order of the efficiencies of the metal ions being $Ca^{2+} < Mg^{2+} < Mn^{2+}$. The maximum efficiency of Mn^{2+} observed in the present study agrees with the report of Wilberg [22] who showed that Mn^{2+} is a protein activator of the enzyme.

Having realized the effect of various metal ions, the next step was to study the concentration effect, taking Mn^{2+} as the representative case. Fig. 5 depicts the effect of [Mn^{2+}] on hydrogen production. A total of 1 mM is found

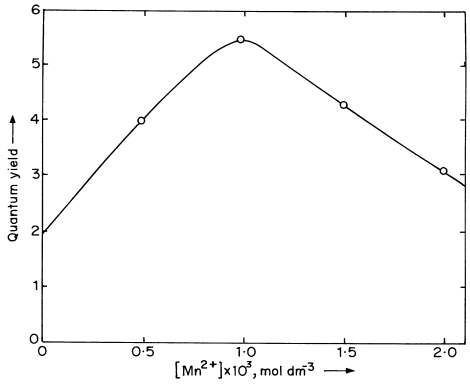


Fig. 5. $[Mn^{2+}]$ variation on photobiocatalytic hydrogen production using 4 at.% Cu(II)/TiO_2/EDTA/*R. capsulata*. [EDTA] = 0.02 M.

to be the optimum concentration. Probably, the activation of the enzyme gets saturated at this concentration of Mn^{2+}. A still higher concentration will lead only to the formation of metal-EDTA complex, which is an unwanted effect, as the electron donor activity of EDTA is reduced.

3.5. Hydrogen production with CdS/TiO_2/MV^{2+}/electron donor/R. capsulata

TiO_2 gets sensitized by mixing with low-band gap semiconductor, e.g., CdS. Hydrogen production was attempted with CdS-loaded TiO_2 and the results (Fig. 6) indicate that CdS-loading improves the photocatalytic efficiency of TiO_2. This was ascribed [9] to a more efficient charge separation caused by the inter-particle electron transfer from the conduction band of excited CdS to conduction band of TiO_2. The transferred electron has sufficient energy to reduce MV^{2+} to MV^{+}, which then undergoes the usual process, producing hydrogen in the presence of the enzyme catalyst. Scheme 3 illustrates the pathway involved in hydrogen production.

In Scheme 3, e^-_{CB} of CdS is utilized for hydrogen production, while the hole is scavenged by EDTA. In this process, EDTA acts as a hole scavenger to prevent photocorrosion of CdS. Addition of Mn^{2+} to the system, as before, increases the amount of hydrogen production.

3.6. Comparison of different catalytic systems

If 1 h is considered as the unit time comparison, then naked TiO_2 produced 0.7 ml/h of hydrogen in the presence of MV^{2+}, electron donor, and bacterial cells. Under similar conditions, the sensitized TiO_2, whatever may be the type of sensitization produced 1.1–1.2 ml/h of hydrogen, if $Ru(bpy)_3^{2+}$ and Rhodamine B are excluded from the list of photosensitizers. If these are also included, then dye-sensitized TiO_2 stands first among the different types of catalysts around the twofold increase in hydrogen production.

Of all the catalyst systems investigated, Mn^{2+}, with Cu(II)/TiO_2, produced the highest amount of hydrogen (1.8 ml/h) followed by Rhodamine B sensitized TiO_2 (1.6 ml/h). If Mn^{2+} is also included in the latter system, it may, perhaps, coincide with the efficiency of the former. If stability, coupled with efficient activity, is adopted as the factor for comparison, then Cu(II)/TiO_2 is a more durable system than others especially for continued irradiation, since others have the possibility (dyes as well as CdS) to deteriorate on long exposure to light which is not shown in figures and tables because it is a well known phenomena.

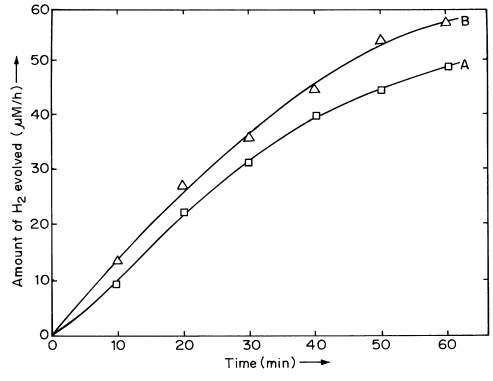


Fig. 6. Photobiocatalytic hydrogen production using 10% *w*/*w* CdS/TiO_2/EDTA/*R. capsulata*. [EDTA] = 0.02M. (A) without Mn^{2+} ion addition, (B) with Mn^{2+} ion addition.

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