

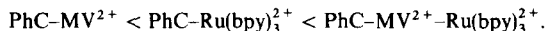


VISIBLE LIGHT-INDUCED HYDROGEN PRODUCTION FROM WATER WITH Pt/Bi₂O₃/RuO₂ IN PRESENCE OF ELECTRON RELAY AND PHOTSENSITIZER

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Abstract—An attempt is made to prepare Pt/Bi₂O₃/RuO₂ (PhC) catalyst and to use it for photocatalytic production of hydrogen from water in the presence of: (i) methyl viologen (MV²⁺) as an electron relay, (ii) Ru(bpy)₃²⁺ as a photosensitizer, or (iii) both (i) and (ii) with visible light of $\lambda \geq 400$ nm. Compared to the undoped γ -Bi₂O₃, the above catalyst is more efficient in hydrogen production. The efficiencies of the different systems constituted by the catalyst with MV²⁺ or Ru(bpy)₃²⁺ or both, in hydrogen production are in the order



Suitable explanations and plausible mechanisms and schemes have been provided to account for the observations in each category of the experiment.

INTRODUCTION

Hydrogen production from cheap raw materials like water is a challenging project that could provide a solution for future energy needs. Among the different approaches photocatalysis has received attention as a possible method for photochemical conversion and storage of solar energy [1–4]. Semiconductors act as photocatalysts generating e_{CB}^- and h_{VB}^+ for the cleavage of water into hydrogen and oxygen. Oxide semiconductors play a prominent part in photocatalysis because of their resistance to photocorrosion. However, most of them have wide band gaps and exhibit a very little absorption in the visible region. They can, however, be sensitized either by doping/loading with transition metal ions or by using external photosensitization with organic dyes such as phenothiazine, rhodamine B, Rose bengal, etc., and by an inorganic dye (complex), Ru(bpy)₃²⁺.

Among the various oxide semiconductors γ -Bi₂O₃ has received the least attention as a photocatalyst for water splitting, although its band gap energy ($E_g = 2.8$ eV) could provide partial absorption in the visible region. In our previous papers [5, 6], we reported studies with Cu(II)/Bi₂O₃ and using it as a photocatalyst for the visible light assisted decomposition of peroxomonosulphate. We have also achieved visible light-induced hydrogen production with Cu(II)/Bi₂O₃ and Pt/Bi₂O₃/RuO₂ from aqueous methyl viologen solution [7]. In this paper we report on studies on the capability of γ -Bi₂O₃ loaded with Pt and RuO₂ and sensitized externally with

Ru(bpy)₃²⁺ to photocatalyse the cleavage of water into hydrogen and oxygen in the presence or absence of an electron relay, MV²⁺. The combined effect of photosensitizer and electron relay on the activity of the bifunctional redox catalyst Pt/Bi₂O₃/RuO₂ has also been investigated.

EXPERIMENTAL

Materials

Semiconductor grade Bi₂O₃ powder (99.99%) was obtained from Fluka (Switzerland). H₂PtCl₆ and RuCl₃ were from John Matthey Chemicals Ltd (U.K.) and methyl viologen was from Aldrich (U.S.A.). All other chemicals used were of research grade.

Ru(bpy)₃Cl₂ preparation

We refluxed 2,2'-bipyridyl (2.0 g, 25% excess) and RuCl₃·3H₂O (0.7 g) in 95% ethanol [8] for 72 h. At the end of this time the dark orange-red solution formed was filtered, evaporated to a small volume and extracted with benzene. Ru(bpy)₃Cl₂ was then precipitated from a dilute aqueous solution by the addition of excess KCl.

Catalyst preparation and procedure for hydrogen production

Pt (0.5% w/w) was loaded on to Bi₂O₃ by the thermal platinumization method and RuO₂ (0.5% w/w) was loaded by high-temperature sintering technique in argon atmosphere [9]. Loading of Pt and RuO₂ was also carried out in an alternative way, i.e. by mechanical mixing of Pt and RuO₂ black with γ -Bi₂O₃.

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The catalysts prepared characterized by XRD, diffuse reflectance spectra and Quantasorb surface area analysis were reported in an earlier paper [7]. The procedure for the measurement of the amount of hydrogen produced was reported earlier [7]. The catalyst (80 mg) was dispersed in 80 ml of the aqueous methyl viologen solution ($[MV^{2+}] = 4 \times 10^{-5} \text{ mol dm}^{-3}$) at 25°C deaerated with argon for 1 h and illuminated with light from 1000 W tungsten-halogen lamp. U.v. and i.r. radiations were cut off using appropriate glass filter and water jacket, respectively. The light intensity of the lamp at 400 nm was determined by potassium ferrioxalate actinometry [10]. Adapting this method, a 0.006 M solution of potassium ferrioxalate was irradiated at 400 nm with the lamp used for hydrogen production experiments and thereby the light intensity of the lamp was found to be $1.65 \times 10^{-8} \text{ einstein s}^{-1} \text{ cm}^{-2}$. The evolved gas was passed through alkaline pyrogallol solution at 0–5°C to remove oxygen (if formed due to water oxidation by $h\nu_{\text{B}}$) as the rest of the gas was collected in a water manometer. The collected gas was detected as hydrogen by GC (Chromatography & Instruments Company, India) using Porapak Q column and argon as the carrier gas.

Estimation of quantum yield

Quantum yields for photocatalytic hydrogen production using undoped/doped Bi_2O_3 were calculated by using the following formula

$$\text{quantum yield } (\phi_{\text{H}_2}) = \frac{2 \times \text{H}_2 \text{ rate (mol s}^{-1}\text{)}}{\text{photon rate (einstein s}^{-1}\text{)}} \quad (1)$$

the denominator in equation (1), is derived as follows, the basic equation of Φ is

$$\Phi = \frac{\text{number of moles formed per unit time}}{\text{number of einsteins absorbed per unit time}} \quad (2)$$

It is seen that from diffuse absorption spectral studies the absorption of different doped samples at $\lambda = 400 \text{ nm}$ differ from one another. Therefore, the actual number of einsteins absorbed from the total number of einsteins coming into the slurry was calculated as

$$\begin{aligned} &\text{number of einsteins absorbed per unit time} \\ &= \frac{\delta I_0 \times \text{absorption at } \lambda = 400 \text{ nm}}{100} \end{aligned} \quad (3)$$

where I_0 is the intensity of the incident light.

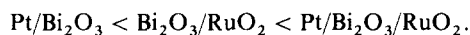
RESULTS AND DISCUSSION

2. Hydrogen production with Pt/ Bi_2O_3 / RuO_2 -photosensitizer system

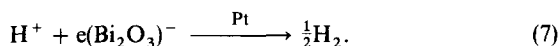
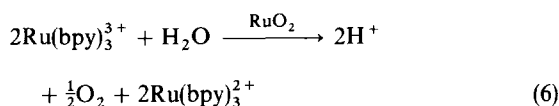
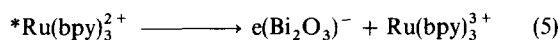
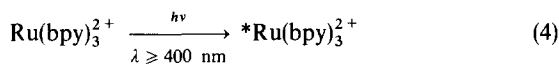
An approach to improve the activity of wide bandgap semiconductor in the visible region involves the use of

photosensitizers (S), which are mostly dyes. Excitation of the dye (S) with visible light radiation results in the injection of electrons to the conduction band of the semiconductor with simultaneous formation of S^+ in solution. Electrons carried through the conduction band cause hydrogen production, while the oxidised dye (S^+) mediates the oxidation of water. For photosensitization, the dye must have its lowest unoccupied energy level above than the conduction band of the semiconductor. $\text{Ru}(\text{bpy})_3^{2+}$ fulfils this criterion as its excited state reduction potential lies at -0.86 V vs SCE which is far higher than the conduction band of most of the oxide semiconductors. To excite $\text{Ru}(\text{bpy})_3^{2+}$, visible light of $\lambda \geq 400 \text{ nm}$ is used and, hence, it is possible to cause photoinduced charge separation. No bleaching of the complex $\text{Ru}(\text{bpy})_3^{2+}$ was observed even with 2 h irradiation in presence of the photocatalyst and MV^{2+} . This is due to the low concentration of the complex which is proved by the UV-VIS spectrophotometrically.

Photosensitization of semiconductors has been studied in detail. For example, high quantum conversion efficiencies of ZnO electrodes deposited with chlorophyll [11], sintered ZnO electrodes sensitized with rhodamine B [12], CdS sensitized with rhodamine B and methylene blue [13] have been reported. In the present work, $\text{Ru}(\text{bpy})_3^{2+}$ is used to photosensitize the catalysts Pt/ Bi_2O_3 , $\text{Bi}_2\text{O}_3/\text{RuO}_2$ and Pt/ $\text{Bi}_2\text{O}_3/\text{RuO}_2$. Table 1 presents the volumes of hydrogen produced with these catalysts but without using MV^{2+} . Their efficiencies for photodecomposition of water are in the increasing order



As observed earlier, here also the bifunctional redox catalyst demonstrates a better role. This is explicable on the basis of the following mechanism. Excited $\text{Ru}(\text{bpy})_3^{2+}$ injects electrons into the conduction band of $\gamma\text{-Bi}_2\text{O}_3$, which are channeled to the Pt site and utilised for the reduction of H^+ to H. $\text{Ru}(\text{bpy})_3^{3+}$ formed is converted back to $\text{Ru}(\text{bpy})_3^{2+}$ by oxidation of water at the oxidation site. The following mechanism is proposed for the photocleavage of water



Scheme 1 depicts all the photocatalytic reactions in an easily understandable manner. The above study has established that hydrogen production from water using

Table 1. Hydrogen production with Pt/Bi₂O₃/RuO₂ using MV²⁺ or Ru(bpy)₃²⁺ or both

Photocatalyst	Volume of H ₂ produced ml h ⁻¹	H ₂ rate × 10 ⁸ (mol dm ⁻³ s ⁻¹)	Photon × 10 ⁸ , ε (s ⁻¹)	Quantum yield (φ)
Pt/Bi ₂ O ₃ *	0.33	0.41	1.54	0.53
Bi ₂ O ₃ /RuO ₂ *	0.39	0.48	1.41	0.69
Pt/Bi ₂ O ₃ /RuO ₂ *	0.59	0.73	1.45	1.01
Pt/Bi ₂ O ₃ †	0.33	0.41	1.54	0.53
Bi ₂ O ₃ /RuO ₂ †	0.33	0.41	1.41	0.53
Pt/Bi ₂ O ₃ /RuO ₂ †	0.60	0.74	1.45	1.01
Pt/Bi ₂ O ₃ /RuO ₂ ‡	0.66	0.82	1.45	1.13
Pt/Bi ₂ O ₃ /RuO ₂ §	0.33	0.41	1.45	0.46

* Using only MV²⁺.

† Using only Ru(bpy)₃²⁺.

‡ Using both MV²⁺ and Ru(bpy)₃²⁺.

§ Prepared by mechanical of Pt and RuO₂ on Bi₂O₃, using only MV²⁺.

[MV²⁺] = 4 × 10⁻⁵ mol dm⁻³; [Ru(bpy)₃²⁺] = 6 × 10⁻⁶ mol dm⁻³; [Pt] = 0.5% w/w; [RuO₂] = 0.5% w/w.

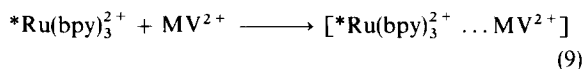
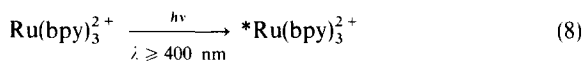
photosensitized semiconductor catalyst is possible even without electron relay as reported already with Pt/Bi₂O₃/RuO₂-Ru(bpy)₃²⁺ system [14].

2. Hydrogen production with

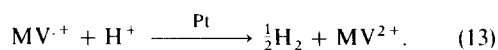
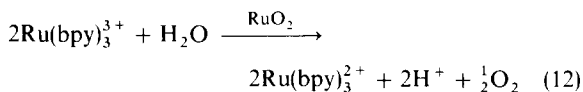
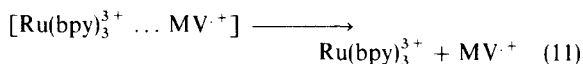
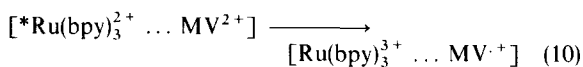
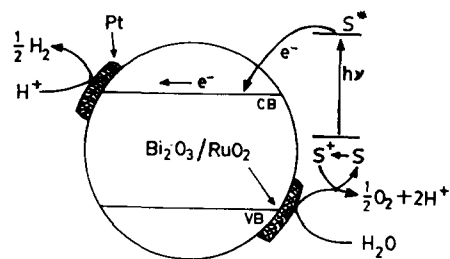
Pt/Bi₂O₃/RuO₂-Ru(bpy)₃²⁺-MV²⁺ system

The present work has confirmed that the bifunctional redox catalyst Pt/Bi₂O₃/RuO₂ mediates photocleavage of water in the presence of MV²⁺ on irradiation with visible light of λ ≥ 400 nm or in the presence of Ru(bpy)₃²⁺. The volumes of hydrogen produced and quantum yields in these two cases are given in Table 1. The actual quantum yield for hydrogen production is less than the theoretical value of two because of losses through scattering, reflection, etc., of the incident light by the photocatalyst. It is of interest, then, to study the combined effect of electron relay and photosensitizer on photocatalytic decomposition of water with the same catalyst with light of λ ≥ 400 nm. The volume of hydrogen produced in this case is 0.66 ml h⁻¹ which is higher than the volume produced (0.60 ml h⁻¹) with photosensitizer alone.

Since the reaction mixture contains both the electron relay and sensitizer, it is but logical that the mechanism involves the coupling of these species. Ru(bpy)₃²⁺, on excitation with visible light, transfers an electron to MV²⁺ adsorbed on the surface of the semiconductor and reduce it to MV^{•+} getting itself oxidized to Ru(bpy)₃³⁺. Ru(bpy)₃³⁺ oxidizes water and returns to its original state, as proposed on scheme 1. Similarly, MV^{•+}, after reducing H⁺ to H₂, gets back to MV²⁺ state. The various reactions involved in the entire process are as follows:

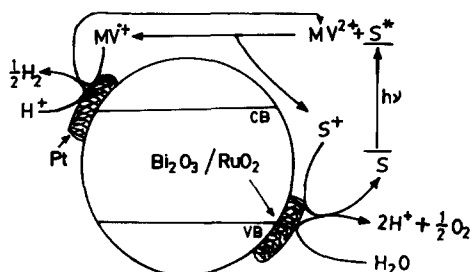


Scheme 1: Hydrogen production with Pt / Bi₂O₃ / RuO₂ - Ru(bpy)₃²⁺ system



Scheme 2 illustrates the photochemical reactions occurring at the surface of the semiconductor catalytic sites. In the above mechanism, electron transfer from the sensitizer to the electron relay is very crucial. Such an electron transfer would be fruitful only when the concerned species, i.e. Ru(bpy)₃²⁺ and MV²⁺ are in close proximity at the surface of the semiconductor. Thus, the role of the semiconductor as a supporting material for

Scheme 2: Photocatalytic cleavage of water with
Pt / Bi₂O₃ / RuO₂ - Ru(bpy)₃²⁺ - MV²⁺ system



adsorption of the redox species and for Pt and RuO₂ deposits as hydrogen and oxygen evolution catalysts respectively is very important in this type of mechanism. This suggestion is supported by the observation that the system Ru(bpy)₃²⁺-MV²⁺-Pt colloid also produced hydrogen under the same conditions but to a lesser extent only (0.46 ml h⁻¹). Thus the adsorption of redox species is an essential requirement for charge separation. An earlier study [15] has also suggested a similar mechanism in the Pt/Bi₂O₃/RuO₂-sensitizer-electron relay. Even though the operation of scheme 2 cannot be totally

excluded, this may occur only to a lesser extent since the [MV²⁺] employed is seven times greater than [Ru(bpy)₃²⁺] and under this condition the electron transfer from the sensitizer to MV²⁺ is more probable than to the conduction band of the semiconductor.

3. Effect of varying the catalyst (Pt/Bi₂O₃/RuO₂) amount

Figure 1 depicts the effect of variation of the catalyst amount on photocatalytic hydrogen production using (Pt/Bi₂O₃/RuO₂) with MV²⁺ or Ru(bpy)₃²⁺ or both. Eighty mg of the catalyst suspended in 80 ml of aqueous methylviologen solution is the optimum catalyst amount for maximum hydrogen production. Below or higher than this amount, there is a decrease in the amount of hydrogen produced. This is due to the fact that with increasing catalyst amount from the lower value, the amount of light absorbed by semiconductor particles increases and therefore the rate of hydrogen production also increases. Eventually a point is reached at which all the incident light is absorbed and the rate of hydrogen production can increase no further. Further increase in the amount of catalyst reduces the penetration depth of the incident light. This may well increase the likelihood of losing scattered light to the exterior and in turn account for the reduction in rate of hydrogen production. A still higher amount of catalyst reduces the penetration depth to such a level that the light loss due to scattering is almost constant and hence there is a levelling off of hydrogen production. Thus, the catalyst amount per unit volume of the solution also plays a crucial role in hydrogen production.

CONCLUSION

1. The bifunctional redox catalyst Pt/Bi₂O₃/RuO₂ in presence of the sensitizer Ru(bpy)₃²⁺ in visible light, exhibits a better catalytic efficiency than when used with MV²⁺ alone.
2. When both the sensitizer and electron relay are coupled with Pt/Bi₂O₃/RuO₂, it becomes the best available system of Bi₂O₃ for photocatalytic production of hydrogen from water.

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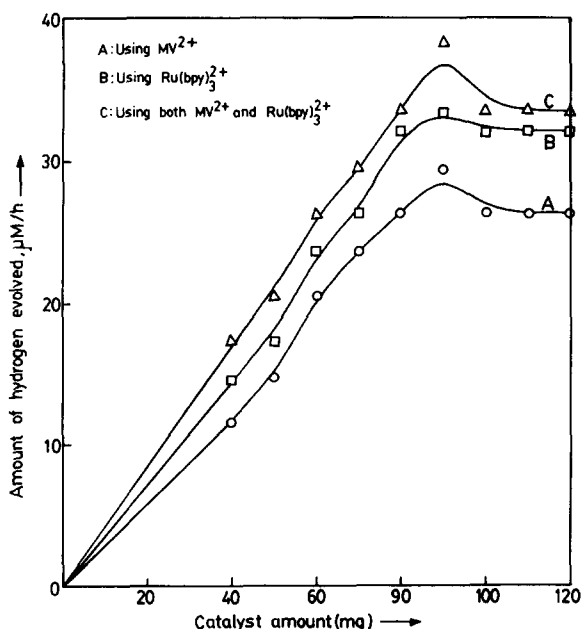


Fig. 1. Effect of catalyst amount (Pt/Bi₂O₃/RuO₂) variation on photocatalytic hydrogen production. (A) using only MV²⁺, (B) using only Ru(bpy)₃²⁺, (C) using both MV²⁺ and Ru(bpy)₃²⁺.

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