

VISIBLE LIGHT INDUCED HYDROGEN PRODUCTION WITH Cu(II)/Bi₂O₃ AND Pt/Bi₂O₃/RuO₂ FROM AQUEOUS METHYL VIOLOGEN SOLUTION

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Abstract— γ -Bi₂O₃, a rarely studied oxide semiconductor, was doped individually with Cu(II) in different concentrations, Pt and RuO₂ (0.5 wt%) and used as a fine powder for photocatalytic production of hydrogen from water in the presence of methyl viologen (MV²⁺) as an electron relay. The diffuse absorption spectroscopy of the samples revealed that the doping process improved the absorption of γ -Bi₂O₃ in the visible region while the XRD spectra indicated no change in crystal structure, but an enhancement in crystallinity. For 90 min irradiation ($\lambda \geq 400$ nm) of the aqueous slurry of the catalyst in presence of MV²⁺, 0.79 and 0.66 ml of hydrogen were generated by 4 at% Cu(II)/Bi₂O₃ and Pt/Bi₂O₃/RuO₂ respectively. A suitable mechanism involving the reactions of photogenerated e⁻ and h⁺ has been proposed for the photodecomposition of water. The effects of dopant concentration and the catalyst amount on hydrogen production have also been explained.

INTRODUCTION

A great deal of research on the conversion of solar to chemical energy has been directed towards the development of photocatalytic systems capable of splitting water into hydrogen and oxygen [1]. The cleavage of water has been achieved by photocatalytic [2] and photoelectrochemical [3] means. In all these researches, it is emphasized that semiconductors with band-gap energies matching the solar spectrum could play a prominent role, as they are able to act as photocatalysts for the cleavage of water into hydrogen and oxygen in the presence of an electron relay, e.g. methyl viologen (MV²⁺). A serious problem associated with such semiconductors, for example, the chalcogenide semiconductors (CdS; $E_g = 2.4$ eV) is their inherent instability [4], because these semiconductors are subject to undesirable photocorrosion by the formed h⁺ itself upon irradiation. The oxide semiconductors (e.g. WO₃, Fe₂O₃ and TiO₂ etc.), on the other hand, have exceptional stability both in acidic and alkaline media [5], but their disadvantage is their band-gaps are usually so wide that they absorb only a very small portion of the solar spectrum. Hence, in order to make them good light-absorbing catalysts, they must be sensitized "internally" by doping with transition metal ions or some external photosensitizer such as Ru(bpy)₃²⁺ must be used.

Copper(II)-doping is particularly attractive [6–8] because it sensitizes the semiconductors to absorb more light in the visible region as well as enhancing their catalytic efficiency through its ability to trap e_{CB}⁻ and to transfer it efficiently to the adsorbed redox species.

Similarly, Pt [9] and RuO₂ [10] are also well known for their pronounced effect in improving the catalytic activity of the semiconductors. In the present work, we choose γ -Bi₂O₃ ($E_g = 2.8$ eV) which is a rarely studied oxide semiconductor. Since this also has a wide band-gap, it is sensitized by doping with Cu(II) ions or loaded with Pt and/or RuO₂. This article describes our findings for the photocleavage of water into hydrogen and oxygen with visible light.

EXPERIMENTAL

Materials

Semiconductor-grade (99.9%) Bi₂O₃ powder was obtained from Fluka. H₂PtCl₆ and RuCl₃ (99%) used for loading purposes were received from Johnson Matthey Chemicals Ltd., England. Methyl viologen, MV²⁺ (1,1'-dimethyl 4-4'-bipyridinium dichloride) was from Aldrich. All other samples used were of research-grade quality chemicals.

Catalyst preparation

γ -Bi₂O₃ was doped with Cu(II) (1–10 at%) by a high-temperature sintering method (400–500°C) in an Ar atmosphere. Platinum (0.5 wt%) was loaded onto the surface of Bi₂O₃ by a thermal platinumization method [11] and RuO₂ (0.5 wt%) by the sintering method. Photocatalysts were prepared by sintering at high temperature in an inert atmosphere as follows: calculated amounts of chlorides of

Cu^{2+} , Pt^{4+} or Ru^{3+} were dissolved in water and mixed with $\gamma\text{-Bi}_2\text{O}_3$ powder by stirring with a magnetic stirrer. The slurry was dried in an air oven at 110°C . The dried sample was transferred to a silica boat and heated in a muffle furnace at $400\text{--}500^\circ\text{C}$ in an Ar atmosphere for 8 h. Then the silica boat was cooled slowly to room temperature and the samples were ground to a fine powder and used for photocatalytic experiments.

Characterization

The diffuse absorption spectra of all the catalysts prepared were recorded (Hitachi spectrophotometer) against a high-alumina plate as the reference. The surface areas of the catalysts were measured with a Quantasorb surface area analyser and the values are in the range $3\text{--}4\text{ m}^2\text{ g}^{-1}$. The undoped and Cu(II)-doped $\gamma\text{-Bi}_2\text{O}_3$ powders were also characterized by the XRD method. (Phillips X-ray powder diffractometer, PW 1130; radiation CuK_α , $\lambda = 1.5418\text{ \AA}$.)

Procedure for hydrogen production

In all the experiments (except for the variation of catalyst amount), 80 mg of the catalyst powder was dispersed in 80 ml of the aqueous methyl viologen solution ($[\text{MV}^{2+}] = 4 \times 10^{-5}\text{ mol dm}^{-3}$). The light source used was a high-intensity 1000 W tungsten-halogen lamp. The u.v. radiation, if any, was cut off with an appropriate glass filter and the i.r. radiation was eliminated by a water jacket. The reaction vessel was purged with Ar gas for about 30 min before irradiation. The volume of hydrogen was measured volumetrically, after passing the evolved gas through alkaline pyrogallol solution to absorb oxygen. Hydrogen was detected by gas chromatography (GC) using Ar as the carrier gas.

RESULTS AND DISCUSSION

Figure 1 shows the diffuse absorption spectra of the undoped $\gamma\text{-Bi}_2\text{O}_3$, Cu(II)-doped $\gamma\text{-Bi}_2\text{O}_3$ and Pt- and/or RuO_2 -loaded $\gamma\text{-Bi}_2\text{O}_3$. It shows that Bi_2O_3 has only $\sim 20\%$ absorption at $\lambda \geq 500\text{ nm}$, whereas Cu(II)/ Bi_2O_3 or Pt/ Bi_2O_3 has about 50% absorption at 500 nm and the

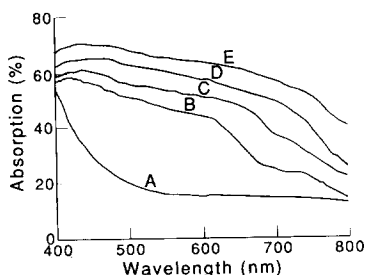


Fig. 1. Diffuse absorption spectra of: (A) undoped $\gamma\text{-Bi}_2\text{O}_3$; (B) 4 at% Cu(II)/ Bi_2O_3 ; (C) Pt/ Bi_2O_3 ; (D) Pt/ Bi_2O_3 / RuO_2 ; and (E) RuO_2 / Bi_2O_3 .

absorption is extended to about 650 or 700 nm in the visible region. Thus, the extent as well as the ranges of absorption of undoped $\gamma\text{-Bi}_2\text{O}_3$ is greatly enhanced by the doping or loading process, due to the phenomenon called "sensitization of the semiconductor" [12]. The XRD spectra of $\gamma\text{-Bi}_2\text{O}_3$ and Cu(II)/ Bi_2O_3 are shown in Fig. 2 and the corresponding "d" spacing and intensity values are displayed in Table 1. The a_0 values calculated from the XRD data are 10.33 and 10.26 \AA , respectively, for $\gamma\text{-Bi}_2\text{O}_3$ and Cu(II)/ Bi_2O_3 which are slightly higher than the theoretical a_0 value (10.10 \AA) of $\gamma\text{-Bi}_2\text{O}_3$ (taken from ASTM). This coincidence absolutely confirms that the crystal structure of $\gamma\text{-Bi}_2\text{O}_3$ is not altered due to Cu(II) doping, but the increase in the spectral intensity resulting from this doping evidently shows that there is an enhancement in crystallinity. Thus Cu(II)-doping causes no detrimental effects in $\gamma\text{-Bi}_2\text{O}_3$, but enhances its absorption.

Hydrogen production with Cu(II)/ Bi_2O_3

Table 2 exhibits the volume of hydrogen produced in 90 min with Cu(II)/ Bi_2O_3 , Cu(II) being doped in different concentrations. Figure 3 shows the rate of hydrogen evolution and it is evident that the hydrogen production is a minimum with the undoped $\gamma\text{-Bi}_2\text{O}_3$, which indicates the poor efficiency of the catalyst. This is an expected observation, because the conduction band of $\gamma\text{-Bi}_2\text{O}_3$, lying close to 0 V, is not cathodic enough to match the water reduction level. In contrast, all the catalysts of doped/loaded $\gamma\text{-Bi}_2\text{O}_3$ show promising trends (Table 2).

With Cu(II)/ Bi_2O_3 for 1 at%, there is a four-fold increase of the volume of hydrogen produced and a 13-fold increase with 4 at% of Cu(II)/ Bi_2O_3 compared with the amount of hydrogen generated with the undoped $\gamma\text{-Bi}_2\text{O}_3$ (0.06 ml/90 min). This enormous increase is due to, as reported earlier [7], the excellent properties of the dopant Cu(II) ion, which has the tendency to raise the conduction

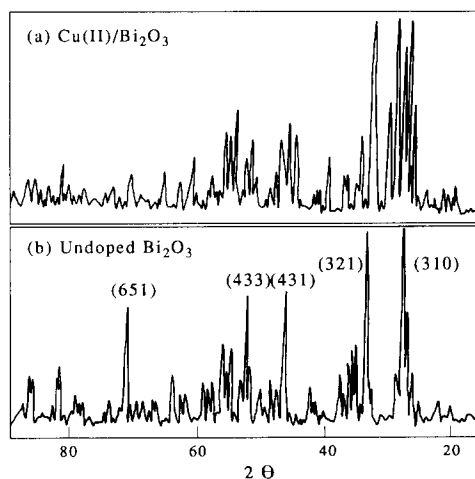


Fig. 2. XRD spectra of: (A) 4 at% Cu(II)/ Bi_2O_3 ; and (B) undoped $\gamma\text{-Bi}_2\text{O}_3$.

Table 1. XRD data*

Theoretical values for $\gamma\text{-Bi}_2\text{O}_3$, $a_0 = 10.10$			Observed values for:			
			Undoped $\gamma\text{-Bi}_2\text{O}_3$ $a_0 = 10.33 \text{ \AA}$		Cu(II)/ Bi_2O_3 $a_0 = 10.26 \text{ \AA}$	
d spacing (\AA)	hkl	I/I_0	d spacing (\AA)	I/I_0	d spacing (\AA)	I/I_0
3.22	100	310	3.27	177	3.25	373
2.17	30	332	2.18	19	2.15	18
1.74	90	433	1.75	96	1.75	61
1.70	40	442	1.68	54	1.67	67
1.65	60	532	1.66	33	1.64	53
1.50	60	631	1.5	24	1.50	29
1.29	20	651	1.32	87	1.32	25

*Radiation: $\text{CuK}\alpha$; $\lambda = 1.5418 \text{ \AA}$; $2\theta = 10-90^\circ$.

band level cathodically [13] and to scavenge or to trap the conduction band electrons efficiently, thereby preventing $e^- - h^+$ recombination which is a serious handicap in semiconductor photocatalysis. The trapped electrons which reduce Cu(II) to Cu(I), are then transferred from Cu(I) to MV^{2+} , the electron relay adsorbed on the catalyst particle, to form $\text{MV}^{\cdot+}$ which, in turn, reduces H^+ to H. The species Cu(II) and MV^{2+} are generated back in the above consecutive processes which then continue the redox reactions in the same manner, thus constituting a cyclic process for water decomposition. The following mechanism illustrates the above process:

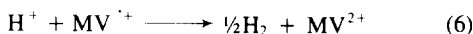
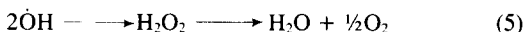
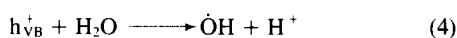
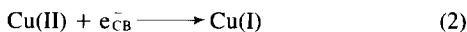
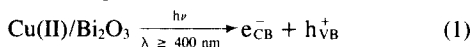


Table 2. Effect of dopant concentration on hydrogen production with Cu(II)/ Bi_2O_3 *

[Dopant] (at %)	Volume of hydrogen produced (ml/90 min)
Undoped	0.06
1	0.26
2	0.53
3	0.66
4	0.79
7	0.46
10	0.26

* $[\text{MV}^{2+}] = 4 \times 10^{-5} \text{ mol dm}^{-3}$.

The simultaneous evolution of oxygen and hydrogen, as proposed in the above mechanism, is confirmed by their detection with oxygen-sensitive electrode and gas chromatography respectively. This mechanism is further supported by the previous reports available in the literature on the formation of the intermediates Cu(I) and $\text{MV}^{\cdot+}$ [14] and on the reduction of H^+ to H by $\text{MV}^{\cdot+}$ [15]. Such electron transfers as these are not possible with undoped $\gamma\text{-Bi}_2\text{O}_3$ and, hence, it possesses the least-efficient catalytic activity.

Effect of dopant concentration on hydrogen production

The effect of increasing Cu(II) dopant concentration on hydrogen production (Table 2, Fig. 3) demonstrates that 4 at% of Cu(II) is the optimum dopant concentration, above or below which there is a decrease in the hydrogen evolution rate. The increasing dopant concentration in the range 1-4 at% enhances the rate, due to the increase in efficiency of transfer of e_{CB}^- to MV^{2+} , i.e. the efficiency of $e^- - h^+$ separation. However, after the optimum level, the tiny semiconductor particle is thickly populated with the dopant centres and, hence, the extent of image force of these centres towards e^- and h^+ also increases, with a consequent band-gap narrowing at the metal-semiconductor interface [16] and, as a result, the $e^- - h^+$ recombination becomes easier at higher dopant concentration. It is obvious from the foregoing discussion that the $e^- - h^+$ separation at higher dopant concentration is not as effective as at lower dopant concentration.

Hydrogen production with Pt/ Bi_2O_3 /RuO₂

Since most of the oxide-semiconductor powders are poor catalysts for hydrogen generation, one often needs metallic deposits so as to reduce the overvoltage requirement for the reduction of H^+ to H. Depending upon the metal and surface characteristics of the semiconductor, a metal-semiconductor contact may give rise to a Schottky barrier, or may just be an ohmic contact [17]. As this barrier would drive e_{CB}^- away from the metal, for the metal deposits to act as better reduction centres, the contact must

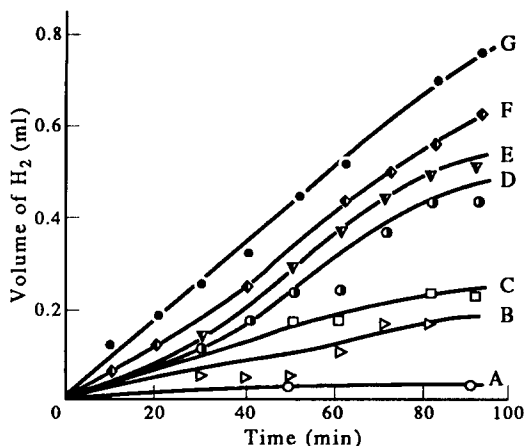
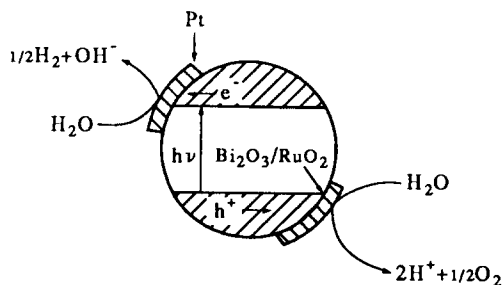


Fig. 3. Rate of hydrogen production with Cu(II)/Bi₂O₃ in methyl viologen solution for: (A) undoped γ -Bi₂O₃; (B) 1 at% Cu(II)/Bi₂O₃; (C) 10 at% Cu(II)/Bi₂O₃; (D) 2 at% Cu(II)/Bi₂O₃; (E) 7 at% Cu(II)/Bi₂O₃; (F) 3 at% Cu(II)/Bi₂O₃; and (G) 4 at% Cu(II)/Bi₂O₃.

be ohmic. Similarly to metal deposits, one also needs metal-oxide deposits such as RuO₂, Rh₂O₃ or IrO₂ on the surface of the semiconductor catalyst, which behave as hole-transfer agents. In the present work, Pt and RuO₂ were chosen as the metal and metal-oxide deposits respectively for γ -Bi₂O₃.

The volumes of hydrogen produced in 90 min with Pt/Bi₂O₃, RuO₂/Bi₂O₃ and Pt/Bi₂O₃/RuO₂ are 0.33, 0.39 and 0.66 ml, respectively. Compared with 0.06 ml of hydrogen produced with the undoped γ -Bi₂O₃, the above catalysts show better efficiencies. The explanation for this observation is as follows. Platinum loaded onto γ -Bi₂O₃ traps e_{CB} and facilitates the reduction of H⁺ to H₂, owing to its ability to lower the overvoltage of hydrogen production, as well as the point of zero zeta potential [18]. In the case of RuO₂ loading, the RuO₂/Bi₂O₃ junction behaves as a Schottky potential barrier [19] which is of enough height to enhance the oxidizing power of holes. RuO₂ is also known as a catalyst for hydrogen production [20]. Hence, RuO₂/Bi₂O₃ generates a slightly higher amount of hydrogen than does Pt/Bi₂O₃ (the difference is 0.06 ml/90 min). When both the deposits are made, there is a combined effect, the net result being a two-fold increase in the amount of hydrogen production. Scheme 1 depicts the role of Pt/Bi₂O₃/RuO₂ in the photodecomposition of water.

Our observation regarding the effect of Pt and RuO₂ deposits on the photocatalytic efficiency of γ -Bi₂O₃ is supported by previous reports available for other semiconductors. It has been noticed [21] that colloidal CdS loaded with RuO₂ cleaves water without undergoing much photocorrosion during irradiation; However, in the absence of RuO₂, there is a considerable degree of photocorrosion which is a phenomenon of oxidation and, hence, decomposition of CdS by the photogenerated h⁺ itself. The absence of photocorrosion with RuO₂ loading confirms that there is a definite transfer of holes from the surface of



Scheme 1. Photodecomposition of water with Pt/Bi₂O₃/RuO₂.

CdS. Similarly, Gratzel *et al.* [22] have shown that cleavage of water takes place to a considerable extent when colloidal TiO₂ is loaded with RuO₂ and Pt.

Effect of catalyst (Pt/Bi₂O₃/RuO₂) amount variation

The effect of variation of the catalyst amount on the volume of hydrogen evolved is shown in Fig. 4. Eighty milligrammes of the catalyst suspended in 80 ml of aqueous methyl viologen solution is the optimum catalyst amount for maximum hydrogen production. Below or above 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 the semiconductor particles increases and, therefore, the rate of hydrogen production also increases. However, a point is reached eventually at which all the incident light is absorbed and the rate of hydrogen production can increase no further. A 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 the rate of hydrogen production. A further increase in catalyst amount leads to a decrease in the penetration depth of the incident light to such a level that the light loss due to scattering is almost constant and this may then account for the levelling-off of the rate of hydrogen production. Thus, the

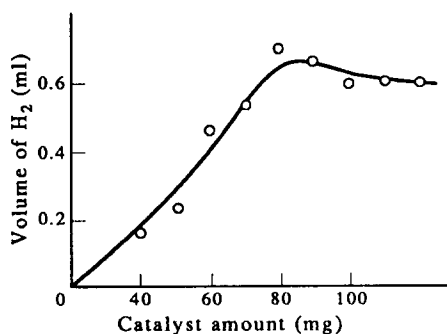


Fig. 4. Effect of catalyst amount variation on hydrogen production with Pt/Bi₂O₃/RuO₂. Catalyst = Pt/Bi₂O₃/RuO₂, [MV²⁺] = 4×10^{-5} mol dm⁻³.

catalyst amount per unit volume of the solution also plays a crucial role in hydrogen production.

CONCLUSION

Although the photocatalytic efficiency of undoped γ - Bi_2O_3 is very low, it is very much enhanced when γ - Bi_2O_3 is doped with Cu(II) or loaded with Pt and/or RuO_2 .

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