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Photocatalytic Activities of Bi_2O_3, WO_3, and Fe_2O_3: An Assessment through Decomposition of Peroxomonosulfate in Visible Radiation

Pichai MARUTHAMUTHU,* Karuppusamy GURUNATHAN, Esaikkiappan SUBRAMANIAN, and Muthupandian ASHOKKUMAR
Department of Energy, University of Madras, A. C. College Campus, Madras 600025, India

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Bi_2O_3 semiconductor powder (E_g=2.8—2.9 eV) was chosen for the first time to effect photocatalysis and was found to decompose peroxomonosulfate (PMS) with visible light of $\lambda > 400$ nm. Doping of Bi_2O_3 with Cu(II)-ion considerably enhanced the photocatalytic efficiency. The effects of variation of (i) the [dopant] in Cu(II)/Bi_2O_3, (ii) the catalyst amount, and (iii) the initial [PMS] on the rate of decomposition of PMS were investigated. It was observed that (a) 4 atomic % was the optimum [dopant] for Cu(II)/Bi_2O_3, (b) the rate increased linearly with increase in catalyst amount, and (c) the decomposition of PMS followed a Langmuir kinetics in the concentration range, $[PMS]_0=0.5—3.0\times10^{-3}$ mol dm^{-3}. A suitable reaction mechanism is proposed for the decomposition of PMS involving all the possible reactions. A comparative analysis of the photocatalytic activities of undoped and Cu(II)-doped Bi_2O_3, WO_3, and Fe_2O_3 indicated that Cu(II)-doping enhances the activity of Bi_2O_3 to a greater extent than those observed with the other two semiconductors. This photocatalytic decomposition of PMS is one of the examples of visible light assisted reaction which otherwise takes place under UV radiation ($\lambda \leqslant 280$ nm) only.

The search for viable means of conversion of solar energy into other forms has gained momentum during the past few years and the role of semiconductors in this aspect has occupied a prominent place.[1] The oxide semiconductors, especially in the form of powders appear to be most promising for photocatalysis because of their inherent advantages such as (1) resistance to photocorrosion,[2] (2) stability in both the acidic and alkaline media, and (3) larger surface area needed for photocatalysis. Many reports on the photocatalytic activities of several oxide semiconductors, TiO_2, ZnO, SnO_2, Fe_2O_3 etc., are already available. Using WO_3, we have recently reported the photocatalytic decomposition of peroxides[3] and the photocleavage of water.[4,5]

Although the investigations with oxide semiconductors are numerous, so far only a few studies with Bi_2O_3 have been reported, despite the fact that the band-gap energy (E_g) of this semiconductor is only 2.8—2.9 eV, which absorbs more solar radiation in the visible region compared to that of either TiO_2 or $SrTiO_3$ with which numerous investigations are available. In studies conducted over the years, Bi_2O_3 has been used as a stabilizing agent and/or as a dopant in solid electrolytes. Kruidhof et al.[6,7] have prepared, characterized, and investigated the mechanical properties of Bi_2O_3-based ceramics. Winnubst and Burggraaf[8] have also prepared and studied the electrical properties of monophasic Y_2O_3-stabilized ZrO_2 doped with Bi_2O_3. In both these studies, it has been reported that the inclusion of Bi_2O_3 enhances the stability of the solid electrolyte. Only one study[9] has been carried out in detail on the photoelectrochemical properties of anodic Bi_2O_3 films. Since investigation dealing with the photocatalytic aspects of Bi_2O_3 semiconductor powder is found absent, the present work which involves the assessment of the photocatalytic activities of undoped and Cu(II)-doped Bi_2O_3 through visible light assisted decomposition of peroxomonosulfate (PMS, HSO_5^-) and comparison of the efficiencies of the above catalysts with those of undoped and Cu(II)-doped WO_3 and Fe_2O_3, are attempted. The findings of this work are significant because they brighten the possibility of Bi_2O_3 application for photocatalysis in future. This study also serves as an example for visible light assisted decomposition of PMS which otherwise happens only by UV irradiation, $\lambda \leqslant 280$ nm.

Experimental

Bi_2O_3, WO_3, and Fe_2O_3 semiconductors (99.9%) were obtained from Fluka. PMS was from E.I. du Pont de Nemours & Co., USA and was used as such. Other chemicals used were of the purest research grade available.

In catalyst preparation, a high-temperature sintering technique was used. The Cu(II)-doped (at different atomic %) semiconductor catalysts were prepared as follows: a calculated quantity of $CuCl_2$ salt (99%) was added to the aqueous slurry of the semiconductor and it was stirred magnetically for 2 hours, dried in an air oven at 110 °C and sintered at 400—500 °C for Bi_2O_3, 700—800 °C for WO_3, and 1200—1300 °C for Fe_2O_3. The sintered samples were then ground to fine powders and stored in light-proof vials. Undoped samples of Bi_2O_3, WO_3, and Fe_2O_3 were also processed in a similar manner at temperatures mentioned above. The surface areas of the catalysts were determined by Quantasorb surface area analyzer and found to be 2.0—3.0 m^2 g^{-1}. The catalysts were also characterized by diffuse reflectance spectra (Hitachi, Japan) and X-ray diffraction methods (Philips, Holland).

A typical procedure followed in the photocatalytic experiment is given below. 40 ml of the PMS solution ($[PMS]_0=0.5—3.0\times10^{-3}$ mol dm^{-3}) in water containing 40 mg of the catalyst was irradiated with visible light of $\lambda>400$ nm from a 150-W xenon lamp (Applied Photophysics, London), after cutting off UV and IR radiations with appropriate glass filter and water jacket, respectively. The experiment was carried out at room temperature (ca. 25 °C) and at natural pH (ca. 6). The [PMS] was estimated iodometrically and the rate was followed by determining [PMS] at various time intervals.

Determination of Quantum Yields. Quantum yields for the PMS decomposition were determined by employing potassium tris(oxalato)ferrate(III) actinometry as described in literature.[10] A range of wavelength (400—450 nm) rather than a single wavelength was selected for this determination, because in this range, all the catalysts have maximum absorption (nearly 60%) and this was taken as an advantage in the photocatalytic experiments. A 0.006 M $K_3[Fe(C_2O_4)_3]$ solution was irradiated with the same 150-W xenon lamp mentioned above, after passing the light through a band filter for the 400—450 nm range. From the amount of Fe^{2+} formed during irradiation, the light intensity of the lamp was determined assuming $\Phi=1.11$. This experiment was repeated by keeping the semiconductor slurry in the light path and from the difference in intensities, the light intensity absorbed by the semiconductor particles was calculated. The quantum yield (Φ) for the PMS decomposition reaction was determined from the relation,

$$\Phi=\frac{\text{Number of moles of PMS decomposed per second}}{\text{Number of Einsteins absorbed per second}}. \quad (1)$$

Results and Discussion

Characterization of the Catalysts. In order to get an idea about the extent of absorption of the undoped and doped semiconductors in the visible region and to know the effect of Cu(II)-dopant on the crystallinity of the semiconductors, the catalysts were characterized by diffuse absorption spectra and X-ray diffraction methods. Figure 1 shows representatively, the absorption spectra of Bi_2O_3 and Cu(II)/Bi_2O_3 catalysts. Bi_2O_3 has 55% absorption upto 410 nm, 40—20% upto 500 nm and about 15% in the remaining part of the spectrum. But when it is doped with Cu(II), the absorption ranges are increased considerably. Similar is the case with WO_3. But with Fe_2O_3, since it is of dark brown color, both Fe_2O_3 and Cu(II)/Fe_2O_3 have relatively more absorp-

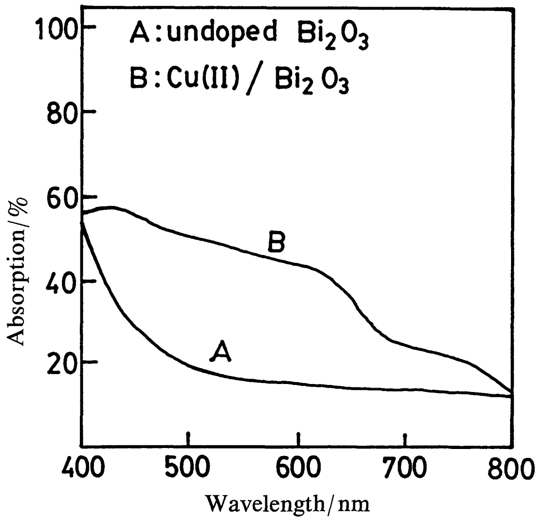

Fig. 1. Diffuse absorption spectra of undoped and doped Bi_2O_3.
A=Undoped Bi_2O_3, B=Cu(II)/Bi_2O_3.

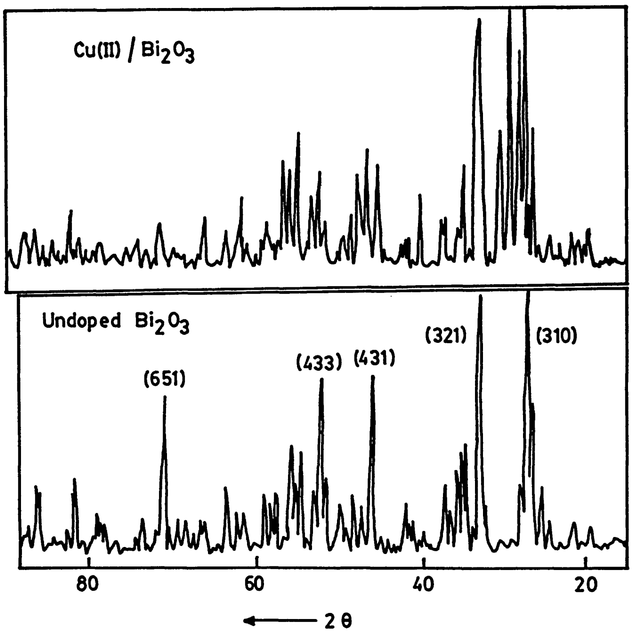

Fig. 2. XRD spectra of Cu(II)/Bi_2O_3 and undoped Bi_2O_3.

Table 1. *d*-Spacing and the Corresponding Intensity Values from the XRD Spectra

hkl Values	Literature values for γ-Bi_2O_3 (a_0=10.10 Å)		Observed values for Bi_2O_3 (a_0=10.33 Å)		Observed values for 4 at% Cu(II)/Bi_2O_3 (a_0=10.27 Å)	
	d/Å	*I*/*I*$_0$	*d*/Å	*I*/*I*$_0$	*d*/Å	*I*/*I*$_0$
310	3.22	100	3.27	177	3.25	373
400	2.54	10	2.54	56	2.56	51
431	2.00	30	1.96	78	1.96	67
433	1.74	90	1.75	96	1.75	61
532	1.65	60	1.66	33	1.64	53
541	1.57	10	1.57	32	1.58	27
631	1.50	60	1.51	24	1.50	29
640	1.41	10	1.40	20	1.41	31
651	1.29	20	1.32	87	1.32	25
800	1.27	10	1.28	13	1.28	13

tion than the other two semiconductors in the entire visible region. Thus in all these semiconductors, doping of Cu(II) increases the absorption in the visible region and this has been already explained[11] as due to the introduction of 'isolated energy levels' by the dopant in the band gap of the semiconductors.

X-Ray diffraction spectra of all undoped and Cu(II)-doped semiconductors, for example, the XRD spectra of Bi_2O_3 and Cu(II)/Bi_2O_3 shown in Fig. 2 with the corresponding 'd' spacings and intensity values given in Table 1, indicate that there is no appearance of any new peaks due to Cu(II)-doping but that the intensities of the peaks are increased, even though both the doped and undoped samples were processed at the same temperature. This observation demonstrates that Cu(II)-doping increases the crystallinity of the semiconductors without affecting the original crystal structure. Thus doping with Cu(II) produces a favorable change in the catalysts by increasing the absorption as well as the crystallinity of the semiconductors.

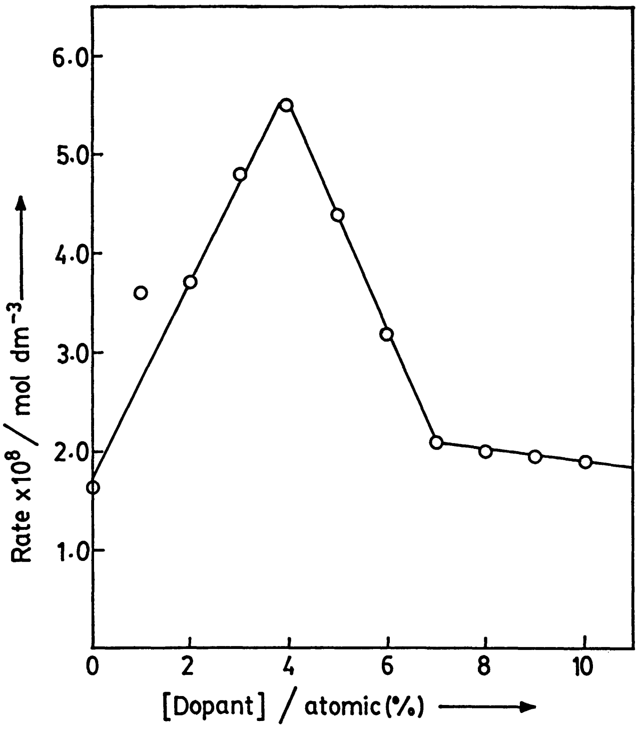

Fig. 3. Effect of variation of [dopant] on decomposition of PMS.
Catalyst (Cu(II)/Bi_2O_3)=40 mg, [PMS]=0.5×10^{-3} mol dm^{-3}, T=298 K.

Table 2. Effect of Variation of Catalyst Amount. Catalyst=4 Atomic % Cu(II)/Bi_2O_3; [PMS]=0.5×10^{-3} mol dm^{-3}

Catalyst amount/mg	Rate$\times10^8$ / mol dm^{-3} s^{-1}
10	5.0
20	5.2
30	5.3
40	5.5
50	5.5
60	5.5
70	5.5

Decomposition of PMS with Bi_2O_3. In the photocatalytic decomposition of PMS, both Bi_2O_3 and Cu(II)/Bi_2O_3 were used as the catalysts. The rate of decomposition of PMS was studied by varying (i) the [dopant], (ii) the catalyst amount, and (iii) the initial [PMS].

Effect of Variation of [dopant]. In our previous study with WO_3,[4] it was established that Cu(II) is an efficient dopant because of its ability to scavenge e^-_{CB} and hence to prevent e^-–h^+ recombination; therefore Cu(II)/WO_3 was found to have higher efficiency than the undoped one. In order to investigate whether the increase in [dopant] continuously enhances the photocatalytic efficiency of Bi_2O_3 or not, experiments were performed with different [dopant]. Figure 3 displays the effect of variation of [dopant] on the rate of PMS decomposition. The rate is increased with increase in [dopant] upto 4 atomic % but gets decreased beyond this limit. Therefore the optimum [dopant] at which Bi_2O_3 acquires maximum photocatalytic efficiency is 4 atomic %. This observation is explicable by the fact that Cu(II) acts as e^-_{CB} scavenger at lower [dopant] but becomes e^-–h^+ recombination centers at higher [dopant], since the distance between two Cu(II) ions becomes shorter than the distance at which the image force to both e^-_{CB} and h^+_{VB} is effective.[12] This type of observation has already been made in our earlier study.[3]

Since 4 atomic % Cu(II)-doped Bi_2O_3 is found to be the most efficient catalyst, this was chosen as the representative one for further experiments to study the effect of other factors on PMS decomposition rates.

Effect of Variation of Catalyst Amount. Table 2 shows the rates observed with different amounts of the catalyst, Cu(II)/Bi_2O_3. There is a small but linear

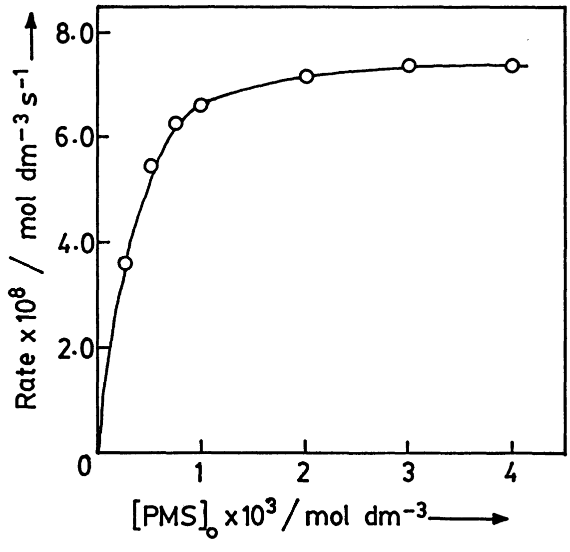

Fig. 4. Plot of rate vs. [PMS]$_0$.
Catalyst=Cu(II)/Bi_2O_3, T=298 K.

increase in the rate with increase in catalyst amount (10—40 mg) which is quite natural since with increase in catalyst amount, the number of catalyst particles coming under the irradiation region increases; in other words the effective surface area of the catalyst responsible for photocatalysis increases leading to the decomposition of more number of PMS molecules and hence the rate is increased. However, further increase of the catalyst amount only results in the saturation limit of the rates.

Effect of Initial [PMS]. The rate of decomposition of PMS was found to be affected by the initial PMS concentrations ($[PMS]_0$) employed in the experiment. From the plot of the rate vs. $[PMS]_0$ (Fig. 4), it is obvious that the rate is increased with increase in $[PMS]_0$ upto a certain range and above that it gets leveled off. This is a typical Langmuirian behavior and hence the effect of $[PMS]_0$ on rate could be described by the following relation,

$$\text{rate} = \frac{kK[PMS]_0}{1+K[PMS]_0} \qquad (2)$$

Where k and K are the proportionality and equilibrium constants respectively. The reciprocal of Eq. 2 gives,

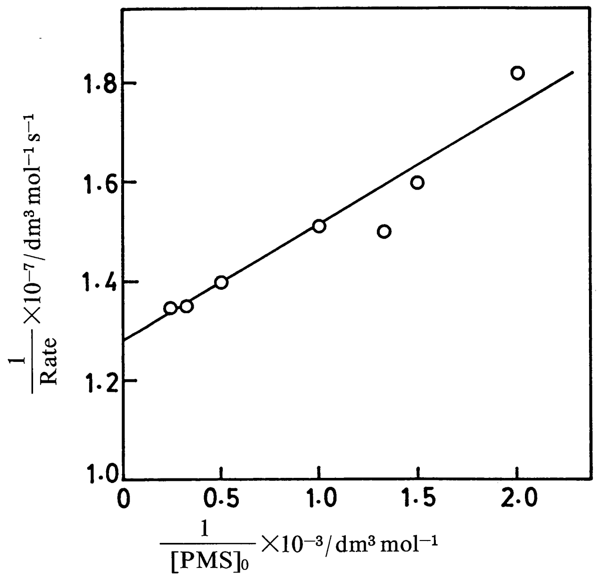

Fig. 5. Plot of $\frac{1}{\text{rate}}$ vs. $\frac{1}{[PMS]_0}$.
Catalyst=Cu(II)/Bi_2O_3, T=298 K.

$$\frac{1}{\text{rate}} = \frac{1}{kK[PMS]_0} + \frac{1}{k} \qquad (3)$$

The plot of 1/rate vs. $1/[PMS]_0$ (Fig. 5) yields a straight line confirming the Eq. 3 and hence it is inferred that the reaction system under investigation obeys a Langmuir kinetics. From the intercept and slope of the plot, in Fig. 5, k and K were calculated and their values are 7.8×10^{-6} mol dm^{-3} s^{-1} and 53.4 dm^3 mol^{-1}, respectively. At lower $[PMS]_0$, since $K[PMS]_0 \ll 1$, Eq. 2 reduces to,

$$\text{rate} = kK[PMS]_0 \qquad (4)$$

This is a first order equation with respect to $[PMS]_0$ and hence it explains the dependence of the rates on $[PMS]_0$ in the initial stages which is evident in Fig. 4. A similar observation on PMS decomposition has been reported.[3]

Reaction Mechanism for PMS Decomposition. PMS is a powerful oxidizing agent (E°=1.82 V). Nevertheless, it acts both as an electron acceptor and hydrogen atom donor which was confirmed by our previous study[13] on the visible-light induced decomposition of PMS with excited state $[Ru(bpy)_3]^{2+}$. Hence there is a possibility that PMS is attacked by both h^+_{VB} and e^-_{CB}. Furthermore it has been established that the hydrated electron (e^-_{aq}) reacts with PMS almost at a diffusion controlled rate.[14] Considering all the above facts, the following mechanism may be proposed for the photocatalytic decomposition of PMS in the presence of a semiconductor catalyst.

$$\text{Semiconductor} \xrightarrow[\lambda>400\text{ nm}]{h\nu} h^+_{VB}+e^-_{CB} \qquad (5)$$

$$HSO_5^- \xrightarrow{\text{Catalyst}} [HSO_5^-]_{ad} \qquad (6)$$

$$[HSO_5^-]_{ad}+e^-_{CB} \longrightarrow SO_4^{\cdot -}+OH^- \qquad (7a)$$

$$[HSO_5^-]_{ad}+e^-_{CB} \longrightarrow SO_4^{2-}+\dot{O}H \qquad (7b)$$

$$2\dot{O}H \longrightarrow 1/2\,O_2+H_2O \qquad (8)$$

$$HSO_5^-+SO_4^{\cdot -} \longrightarrow SO_5^{\cdot -}+HSO_4^- \qquad (9)$$

$$HSO_5^-+\dot{O}H \longrightarrow SO_5^{\cdot -}+H_2O \qquad (10)$$

$$[HSO_5^-]_{ad}+h^+_{VB} \longrightarrow SO_5^{\cdot -}+H^+ \qquad (11)$$

$$2SO_5^{\cdot -} \xrightarrow{H_2O} 2HSO_4^-+3/2\,O_2 \qquad (12)$$

In these equations, $[HSO_5^-]_{ad}$ denotes the PMS molecule adsorbed onto the surface of the catalyst. The formation of $SO_5^{\cdot -}$, $SO_4^{\cdot -}$, and $\dot{O}H$ as the radical products from PMS has been identified by optical pulse radiolysis.[14] Evolution of O_2 during PMS was confirmed by oxygen sensitive electrode and this also serves

Table 3. Rates and Quantum Yields for the Decomposition of PMS with Different Catalysts.
Catalyst Amount=40 mg; [dopant]=4 Atomic % Cu(II); $[PMS]_0=1\times10^{-3}$ mol dm^{-3}

Semiconductor	Undoped Rate$\times10^8$ mol dm^{-3} s^{-1}	Doped with Cu(II) Rate$\times10^8$ mol dm^{-3} s^{-1}	Rate (doped) / Rate (undoped)	Φ (undoped)	Φ (doped)	Φ (doped) / Φ (undoped)
Bi_2O_3	2.3	6.6	2.86	0.9	1.7	1.8
WO_3	2.6	6.6	2.54	1.0	1.3	1.3
Fe_2O_3	3.8	8.7	2.28	0.3	0.8	2.6

as an additional proof for the above mechanism. The overall reaction could be written as:

$$HSO_5^- \xrightarrow[\lambda>400\text{ nm}]{\text{catalyst, } h\nu} 1/2\, O_2 + SO_4^{2-} + H^+ \qquad (13)$$

Efficiency Comparison with Other Catalysts: Experiments were also performed to determine the rates of decomposition of PMS with undoped and Cu(II)-doped WO_3 and Fe_2O_3. For this study, the concentration of PMS used was 1.0×10^{-3} mol dm^{-3} in all cases. Here also the Cu(II)-doped samples exhibit higher activities when compared to the undoped ones. To assign the absolute photoactivity of a particular photocatalyst, the quantum yield is a better candidate than other parameters like rate constants etc. This is because it is an activity parameter which indicates how efficiently a photocatalyst utilizes the absorbed photons for effective photochemical reaction irrespective of the light absorbing capacity of photocatalyst.

Table 3 presents the values of rates and quantum yields for the decomposition of PMS for the doped and undoped samples in the wavelength region 400—500 nm, where all the catalysts have almost equal (about 60%) absorption. By comparing the rates, we have the trend, $Bi_2O_3 \approx WO_3 < Fe_2O_3$ for both doped and undoped samples. But on comparing the quantum yields, the trend becomes, $Bi_2O_3 \approx WO_3 > Fe_2O_3$ for undoped and $Bi_2O_3 > WO_3 > Fe_2O_3$ for doped samples. On comparing the rates and quantum yields of doped and undoped samples, it is clear that both rates and quantum yields have been increased considerably by doping with Cu(II). Even though the rate is higher for Fe_2O_3 when compared with the other samples, the quantum yield seems to be lower due to the fact that the number of photons absorbed by Fe_2O_3 is greater than that absorbed by the other samples. Thus, in spite of having greater light absorbing power, Fe_2O_3 has lower quantum yield value. This is due to the fact that not all the absorbed photons are effectively utilized for PMS decomposition. But with Bi_2O_3 and WO_3, as evident from Table 3, it is the former which gets a maximum increment in activity due to Cu(II)-doping.

Since h^+_{VB} and e^-_{CB} react with PMS, the expected quantum yield for the decomposition of PMS is 2. But in all cases (Table 3) the value is less than 2, even though doping with Cu(II) considerably enhances the quantum yields of the semiconductors. The reasons may be: (i) all the photons entering into the reaction vessel are not absorbed by the catalyst and this may be due to the physical phenomena like reflection, scattering etc., (ii) recombination of a part of the e^-–h^+ pairs formed during irradiation, and (iii) the reversible formation of HSO_5^- from the $SO_4^{\dot{-}}$ and $\dot{O}H$ radicals. In spite of being less than 2, the quantum yields are comparable and retain their identity.

The distinct behavior of Cu(II) with Bi_2O_3 compared to other semiconductors is interpreted as follows. The ionic radius of Cu^{2+} is closer to that of Bi^{3+} in Bi_2O_3 (ca. 0.9 Å) when compare to that of W^{6+} in WO_3 (ca. 0.6 Å). This close similarity in ionic radii of Cu^{2+} and Bi^{3+} is one more advantage which strengthens the inherent nature, i.e. the e^-_{CB} scavenging action of Cu(II). Hence the activity of Bi_2O_3 is enhanced to a greater extent by Cu(II)-doping.

The present study unequivocally reveals that although the undoped Bi_2O_3 is less efficient for photocatalysis, its activity could be improved by Cu(II)-doping to such an extent that Cu(II)/Bi_2O_3 has almost an equal activity to that of Cu(II)/WO_3 which has already found place in photocatalysis.

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