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## **Study of synthesis and photocatalytic activities of Mo doped ZnO**

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### **ABSTRACT**

*The effect of transition metal ions such as Mo (VI) doped ZnO has been investigated for photocatalytic bleaching of eosin Y. Doped samples were synthesized by stirring and microwave exposure. The effect of concentration of dopant on the rate of photocatalytic bleaching of dye has also been observed. The rate of photocatalytic bleaching of dye increases with increase in concentration of dopant up to a certain limit with all these metal ions, but decreases after further concentration of dopants. A tentative mechanism has been proposed.*

**Key words:** Transition metal ions, zinc oxide, photocatalysis, eosin Y.

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### **INTRODUCTION**

Waste water from textile, paper and some other industries contain residual dyes, which are not readily biodegradable. Heterogeneous photocatalysis has been proved to be an efficient technique for the elimination of these pollutants from aqueous and gaseous media [1-3]. Various semiconductors such as TiO<sub>2</sub>, ZnO, ZnS, WO<sub>3</sub> etc. have been used as photocatalyst [4,5]. However, the fast recombination of photogenerated electron and hole pairs slow down photocatalysis. It is great interest to improve the photocatalytic activity of semiconductors for the degradation of dyes in water. ZnO absorbs small portion of visible light and hence, it is necessary to make it efficient by doping so that it can utilize major portion of solar radiations.

Table – 1 Doping with Mo (VI)		
[E] x 10 <sup>3</sup> = 0.50 M	pH = 8.5	
ZnO = 0.12 g	Light Int. = 60.0mWcm <sup>-2</sup>	
Mo (VI) (%)	k x 10 <sup>5</sup> (sec <sup>-1</sup> )	
	Stirring	Microwave
Undoped	6.14	6.14
0.2	7.16	7.82
0.4	7.42	8.93
0.6	8.19	9.49
0.8	6.90	7.81
1.0	6.65	7.61
1.2	6.14	6.68
1.4	5.86	6.68

WO<sub>3</sub> particles were doped with transition metal ions by a high temperature sintering technique [6] while after synthesizing transition metal doped ZnO films, their electrically and magnetically properties have been studied [7,8]. ZnO has been doped by nitrogen, Ni and Co under visible irradiation [9-11]. Degradation of sulphonyl urea herbicide and methylene blue has been carried out by tin doped TiO<sub>2</sub> and Ag-ZnO catalyst, respectively [12, 13]. Optical properties of sulphure doped ZnO nanostructure and Fe doped nanosized TiO<sub>2</sub> have been studied [14, 15].

The quantum efficient of ZnO powder is also significantly larger than that of TiO<sub>2</sub> powder and higher catalytic efficiencies have been reported for ZnO [16]. Pb doped TiO<sub>2</sub> thin films used for photocatalytic microbial inactivation [17]. Change in photocatalytic activity have been investigated over ZnO/ZnO<sub>2</sub> composite [18] and coupled semiconductor which can be formed by different molar ratios such as 1:2 (Z<sub>2</sub>S) and 1:1 (ZS) through coprecipitation method [19]. Transition metal doped TiO<sub>2</sub> particles have been reported by femtosecond to nanosecond spectroscopy [20].

## EXPERIMENTAL SECTION

### 2.1 Sample preparation

Zinc oxide was doped with 4d- transition metal ions such as Mo (VI). The solutions of these transition metal ions were prepared. The weighed amount of ZnO was added to it and the contents were magnetically stirred for about 6.0 hrs to distribute metal ions. Alternately, the doping was also done by keeping the contents under microwave radiation for about 2.0 min. Then ZnO was filtered, washed and dried. Photocatalytic activity of doped samples was investigated by photocatalytic bleaching of eosin Y.

The optical density of this dye was determined with the help of a spectrophotometer (Systronics Model 106) at  $\lambda_{\max} = 510$  nm and the intensity of light at various distance from the lamp was measured with the help of Suryamapi (CEL 201) solarimeter. The rate of reaction of doped samples of zinc oxide was compared with pure sample of zinc oxide.

### 2.2 X- Ray diffraction measurements

For phase identification and confirmation of single phase of the synthesized samples, X-ray diffraction (XRD) studies were carried out at room temperature on a Rigaku Diffractometer that

employed  $\text{CuK}\alpha$  radiation ( $\lambda = 1.54184\text{\AA}$ ) and Bragg-Brento geometry. A silicon sample (cubic  $a = 5.431$ ) was used as a standard sample for internal calibration. XRD patterns for the undoped and doped samples were recorded in the  $2\theta$  range  $10^\circ$  to  $90^\circ$ . The diffractograms were analyzed and indexed with the help of Powder X program. The refinement of the cell parameters was done using least square method. Figure 1 show XRD pattern of doped sample of ZnO.

### Doping

The effect of Mo (VI) doping on the rate of photobleaching of eosin Y has been observed. The results are reported in Table-1. It was observed that as the concentration of Mo (VI) ions increased, more photocatalytic activity was observed in doped samples prepared by microwave irradiation as compared to the samples prepared by stirring. In both; the stirring and microwave methods, activity of doped samples increases up to 0.6 % initially and then, afterwards activity of doped samples declines continuously.

## RESULTS AND DISCUSSION

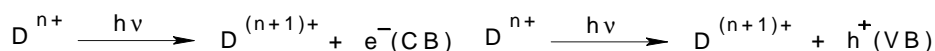
From the above discussion, it may be concluded that the use of dopants like Mo(VI) ions enhance the rate of photocatalytic bleaching of eosin Y. The increase in the photocatalytic activity may be due to introduction of new trapping sites by incorporation of transition metal ions. These sites affect the life time of charge carriers. Since there is high surface coverage of dye, more charge will reach the surface and as a result, the rate of degradation was observed. At higher concentrations, the interstitial sites are completely filled up as a consequence; these sites do not contribute to recombination process. Due to this reason, life time of charge carriers will reduce and fewer charge carriers will reach the surface to initiate the degradation of eosin Y. As a result, the rate of photocatalytic degradation will reduce on increasing the concentration of dopant beyond the limit i.e. 0.6% for Mo (VI).

Samples	Lattice parameters		Unit cell volume ( $\text{\AA}^3$ )	Density $\text{g/cm}^3$
	a ( $\text{\AA}$ )	c ( $\text{\AA}$ )		
Pure ZnO	3.240	5.192	27.251	5.178
ZnO + 0.6% Mo (VI) (MW)	3.254	5.218	27.625	5.109

### 5. Mechanism

Following steps may take place, when transition metal ions doped semiconductor is irradiated with a light of suitable wave length.

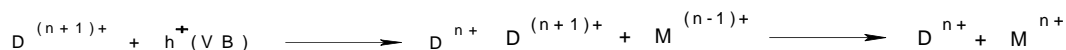
(i) Charge pair generation



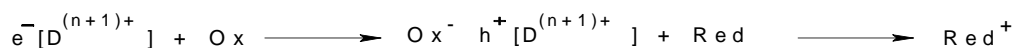
(ii) Charge trapping



(iii) Recombination



(iv) Interfacial electron transfer

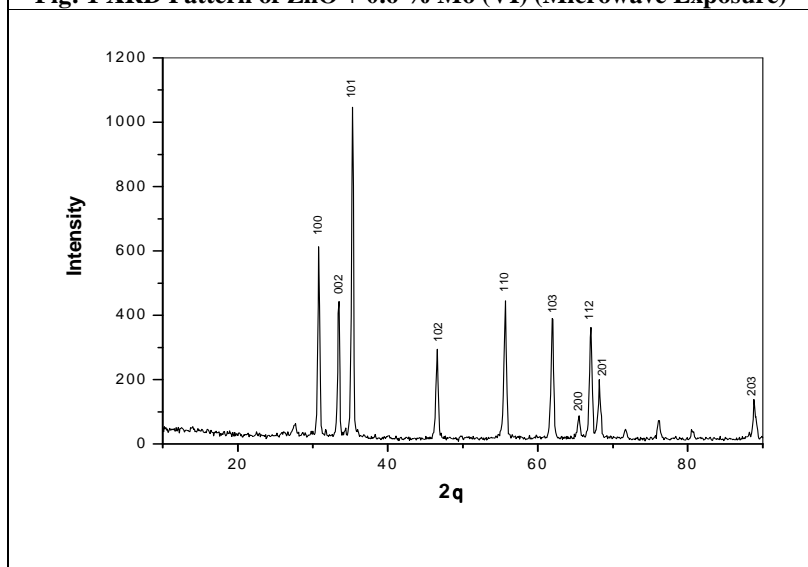


Where  $D^{n+}$ , Red and Ox are transition metal ions used as a dopant, reductant and oxidant, respectively.

### Characterization and crystal structure

Peak No.	2 $\theta$	d-value	h k l	I/I <sub>0</sub>
1	30.800	2.9005	100	58
2	33.500	2.6727	002	41
3	35.300	2.5404	101	100
4	46.600	1.9473	102	28
5	55.700	1.6488	110	42
6	62.000	1.4955	103	37
7	65.500	1.4238	200	7
8	67.100	1.3937	112	34
9	68.200	1.3739	201	18
10	88.800	1.1009	203	13

**Fig: 1 XRD Pattern of ZnO + 0.6 % Mo (VI) (Microwave Exposure)**



None of the step is initiated by  $\bullet OH$  radicals since in presence of  $\bullet OH$  radicals scavenger does not affect rate of degradation. It was observed that the bleaching of the dye can be reverted back on addition of oxidizing agent, but dye does not regain completely the original colour and its intensity, which clearly shows that dye degrades along with its a reduction path.

All the Bragg reflections in the recorded XRD patterns were indexed in the hexagonal ZnO type Wurtzite structure; no other impurity peaks were detected from any other phase. These results confirm single phase formation of the synthesized samples. The refined values of lattice parameters and unit cell volumes along with the estimated values of the density are listed in the Table -2. The obtained values of cell parameters for ZnO (the parent sample used in this study) are in excellent agreement with the reported values. The obtained values of cell parameters for the doped samples are found quite close those reported for ZnO.

### CONCLUSION

The rate of photobleaching of eosin Y over doped zinc oxide powder was more as compare to undoped samples.

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