Synthesis, Structural and Optical Properties of Mn Doped ZnO with its Photocatalytic Activity

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Metal oxides have emerged as one of the most interesting materials under the Green banner due to its potent catalytic properties. Especially, the II-VI metal oxides are gaining considerable attention in optoelectronics and in rectifying environmental issues due to their ability to produce charge carriers when accelerated with sufficient amount of energy. Zinc oxide and $\text{Mn}_x\text{Zn}_{(1-x)}\text{O}$ were synthesized by co-precipitation method. We present a study of effect of doping on the structural, optical and photocatalytic properties of ZnO. The mean particle size was found to decrease from 20 nm to 11 nm and band gap (E_g) increased from 3.25 eV to 3.68 eV with the increase of doping concentration. This increase in E_g might be ascribed to the alteration of electronic arrangement of ZnO nanoparticles on doping with Mn ions. Photocatalytic reduction was conducted in a home-built reactor assembly and degradation of Cr(VI) to Cr(III) under the presence of UV LED was characterized. In the current work, 15 mol % of Mn doped ZnO ($\text{Mn}_{0.15}\text{Zn}_{0.85}\text{O}$) nanoparticles showed the better UV response as compared to the other samples. The strong UV response is due to the more 3d orbitals in the valence band owing to an excess amount of Mn dopants in ZnO nanoparticles. The increase in doping concentration of Mn accelerated the photo catalysis. This result indicates that the concentration of Mn is important in controlling the UV response of the samples. The obtained results reveal that both ZnO and $\text{Mn}_x\text{Zn}_{(1-x)}\text{O}$ are promising materials as photo catalysts.

Keywords: Metal oxide semiconductor, Chromium, Crystallite size, Photocatalytic activity.

INTRODUCTION

Industrial development is an inevitable factor in the growth of any nation and on the other hand it's also the factor for increasing the pollution caused from hazardous metals [1]. Irrelevant of whether advanced or not, the problem faced by almost all sectors of every country is the rottenness caused mainly by ground water contamination, air pollution in large scale and hazardous metal wastes. Chromium is a metal that has found its place in the industrial area with its wide application in electroplating, tanning, refractory materials, wood preservatives and many more [2] but it has also received biological attention due to its major role in contributing to the industrial pollution and its toxicity to plants and animals [3]. The existence of Cr is in two states, *i.e.*, trivalent and hexavalent chromium. The hexavalent form of chromium is 500 times more toxic than the trivalent form [4]. Chromium(VI) and its compounds are highly toxic when inhaled or ingested. It is hemotoxic, genotoxic and carcinogenic. When hexavalent

chromium enters the bloodstream, it damages blood cells by causing oxidation reactions. This oxidative damage can lead to haemolysis and, ultimately, kidney and liver failure. Patients might be treated with dialysis, whereas trivalent chromium is a trace mineral that is essential to human nutrition. Industrial sources release Cr(VI) in effluent streams and should immediately be treated before combining with ground water. The removal of Cr(VI) can be done through various means such as ion exchange [5], adsorption [6] and electrocoagulation [7]. Another alternative for the degradation of Cr(VI) is photocatalytic reduction with semiconductors like ZnO under irradiation with UV or visible light [8].

Semiconductor photo catalysis is a newly advanced oxidation process and is suitable for the degradation of pollutants. Zinc oxide is a semiconductor existing in cubic zinc blende, cubic rocksalt and hexagonal wurtzite structure [9]. Wide direct band gap ($E_g \sim 3.7$ eV) and high exciton binding energy (60 MeV) along with the bulk availability as single crystal make ZnO a good aspirer for optoelectronic devices [10,11] and it

has made a great impact in the fields like biosensors [12] and UV light emitters [8]. The pertinence of semiconductors like TiO_2 , ZnO , Fe_2O_3 , CdS and ZnS is due to the electronic structure of the metal atom in chemical combination, where the electronic structure is constituted by a filled valence band (VB) and an empty conduction band (CB). One of the greatest advantages of ZnO is that it absorbs a large margin of UV spectrum compared to TiO_2 and the corresponding threshold of ZnO is 425 nm [13]. Zinc oxide is reported highly stable under high energy radiation [9]. Numerous experimental attempts have been made to alter its properties for wide variety of functionalities. Recently, introduction of band gap engineering [14] into II-VI semiconducting materials has gained much more consideration due to its excellent structural, optical, electrical, photocatalytic and magnetic properties [14-18]. Band gap engineering can alter the electronic band structure in the desired form by changing the composition of semiconductors with doping. Also, tailoring and tuning the E_g by the introduction of transition metal ions into the cationic metal sites of the host lattice has earned much more consideration in the recent few years. Band gap engineering is a powerful and indispensable tool to be performed for the design of new photocatalytic semiconductor materials and their applications [19,20]. This can be done through doping and alloying ZnO with transition metals. In the course of doping, the ionic radius of dopant should be nearly equal to that of Zn ion so that the replacement of Zn ions by dopants does not change the lattice constant of host crystal significantly. The radius of Mn^{2+} is comparatively [21] close to the radius of Zn^{2+} . Hence, the Mn is assumed to be a profound donor in ZnO . Many research groups have examined the properties of ZnO powder and ZnO doped with selected transition metal ions [19-22]. The preparation method and the ambient conditions affect the characteristic properties of metal oxide semiconductors. Different methods of synthesis such as hydrothermal [22], sol-gel [23], co-precipitation [24], combustion [25], solvo-thermal [26] *etc.* are used to prepare doped and undoped ZnO . Out of these, co-precipitation synthesis is of low cost and eco-friendly.

Of late, the significant interest in UV/light induced chemical reactions on the transition metal-doped ZnO in slurry is increasing. The studies are fewer in number and therefore the effect of dopant on ZnO is still ambiguous [22,27]. A group of researchers reported that the photocatalytic activity, upon irradiation with UV of $\text{Mn}_x\text{Zn}_{(1-x)}\text{O}$ increases up to $x = 2 \text{ mol } \%$. On the other hand, some group have reported inversely [28]. Moreover, it is a simple technology for detoxification of water, eliminating all types of contaminants and in destroying many viruses on the illumination of UV/light under ambient conditions. The establishment of photo catalysis as an effective method for reducing the toxicity of organic compounds and hazardous inorganic constituents and also for the bacteria disinfection of air and water has been progressed in a large scale [29]. The photocatalytic property of ZnO has been proved dynamic [1]. These photocatalytic semiconductors have E_g in the UV region. The photocatalytic property will enact after getting illuminated by UV light rays. Natural light is not a dependable source to observe photo catalysis since the solar spectrum contain 46-47 % of visible and infrared radiation

and just 5-7 % of UV light [30]. Therefore, external supply of UV should be used. This can be an effective measure in reducing the hazardous effect on the environment.

From the semiconductor-photochemistry point of view, the role of a photo catalyst is to accelerate specific chemical redox reaction in the presence of irradiated semiconductors. When a photon of energy $\geq E_g$ of a semiconductor catalyst is used, an electron is promoted from valance band to conduction band leaving a hole behind [31]. The electron which is in the conduction band may photo catalytically reduce the organic pollutant. The conventional photocatalytic reactors are classified into many types like flat plate reactors, honeycomb monolith reactors *etc.* [32] which requires high intensity UV light and the high cost of these conventional reactors is another factor which denies the easy access to a platform for photo catalysis. In the industrial sector, installation cost of such photocatalytic reactors is very high and main problem associated with these reactor configurations is the issue of scale-up for commercial use [33]. A photo reactor that is designed to overcome these deficiencies would be a welcome change. In this paper we introduce a new photoreactor (built in-house) with UV LED strip as the light source. This is very much cost-effective while comparing with the conventional photocatalytic reactors. Simultaneous monitoring of multiple analyses can be easily done in this system. Also, $\text{Mn}_x\text{Zn}_{(1-x)}\text{O}$ nanoparticles were synthesized using an inexpensive simple chemical co-precipitation method and its structural and optical properties have been studied. The photocatalytic reduction of Cr(VI) is studied using $\text{Mn}_x\text{Zn}_{(1-x)}\text{O}$ in a self-designed photocatalytic reactor.

EXPERIMENTAL

The materials used are zinc sulphate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$), sodium hydroxide, cetyl trimethylammonium bromide (CTAB), manganese acetate [$\text{Mn}(\text{CH}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}$], oxalic acid ($\text{C}_2\text{H}_2\text{O}_4$), 1,5-diphenylcarbazide (DPC), deionized water, nitric acid (HNO_3), ethanol ($\text{C}_2\text{H}_5\text{OH}$, > 99 %), isopropyl alcohol ($\text{C}_3\text{H}_8\text{O}$) and Whatman No. 40 filter paper. All the chemicals were of purity $\geq 98 \%$ and were obtained from Sigma-Aldrich and the chemicals were used as received, without any further purification.

Preparation of doped and undoped ZnO nanoparticles: Nanoparticles of $\text{Mn}_x\text{Zn}_{(1-x)}\text{O}$, where $x = 0, 0.05, 0.10$ and 0.15 , were synthesized by chemical co-precipitation method [24,34]. To 100 mL solution of 11.50 g of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and 0.5 g of CTAB, 100 mL solution of NaOH was added slowly with constant stirring using a magnetic stirrer. The stirring was continued for 2 h to ensure homogenous distribution. The white suspension obtained was centrifuged at 3150 rpm for 25 min and washed four times with distilled water and finally washed with acetone. It was then sonicated for 25 min at room temperature. The precipitate was separated by filtration and calcined at 200°C for 2 h. Similarly, the doped samples were prepared. Here, the solution of NaOH is added to the solution containing both $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Mn}(\text{CH}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}$.

Photo reactor assembly: The assembly of self-designed homebuilt photocatalytic reactor is shown in Fig. 1 (line diagram). The photoreactor is built in-house, with a clear objective of achieving a cost-effective and easily assembled

unit, for simultaneous monitoring of multiple analyses. The housing of the unit was made of galvanized sheet which was hammered down to a neat cabin of 2' × 1' × 2' dimensions. The cabin was fit with a door of same material to enable easy handling of the sample. The inside of the cabin, including the door, was decorated with 2" thermal insulation with proper rubber beadings to win a compact setting and minimize any heat loss that may occur during operation. The inner side of the cabin was cemented with a UV LED strip (150 V-265 V AC input, power 0.2 W) in series of three tiers of equal dimensions. No strip was affixed on the roof of the cabin in order to avoid any discomfort. A magnetic stirrer was placed inside the cabin to agitate the contents of the 100 mL beaker, which was used as the reactor. The open beaker attracted maximum radiation and the thin walls facilitated in this action. The whole of the cabin was maintained at a static temperature of 296 K with the help of an insulated-ducted air-heat exchanger of 300 kcal/h capacity. This profusely helped to sufficiently cool the reactor and maintain uniform temperature distribution without any gradient formation.

Fig. 1. Line diagram of photocatalytic reactor

Photocatalytic study: The photocatalytic activity of $\text{Mn}_x\text{Zn}_{(1-x)}\text{O}$ nanoparticles was studied following the degradation of Cr(VI) into non-toxic Cr(III). This degradation was carried out applying UV light from an external source of UV LED strip.

Characterization: The structures of doped and undoped ZnO were analyzed using X-ray diffraction instrument, Philip PW1700, with Cu K α of wavelength $\lambda = 1.5405 \text{ \AA}$. The photocatalyzed reduction of Cr(VI) to Cr(III) was followed by UV-visible-diffuse reflectance spectra using JASCO UV-Vis NIR spectrometer (V-670).

RESULTS AND DISCUSSION

The crystal structure of the samples was characterized by X-ray diffraction technique. The XRD of prepared ZnO nanoparticles is as given in the Fig. 2. The peaks observed at 31.7° , 34.25° , 36.18° , 47.43° , 56.42° , 62.6° and 67.9° indicate that the samples are highly crystalline. Comparing with JCPDS data 36-1451, lattice planes are identified as (100), (002), (101), (102), (110), (103) and (112), respectively, indicating hexagonal wurtzite structure of ZnO. The broadening of the peaks gives an idea about the small particle size of the synthesized ZnO.

Fig. 2. XRD of as prepared ZnO nanoparticles

The average crystallite size (D) was calculated using the Scherer's formula [14] given below:

$$D = \frac{0.89\lambda}{\beta \cos \theta}$$

here, λ and β is the full width at half maximum (FWHM). The crystalline size calculated for the as prepared samples of $\text{Mn}_x\text{Zn}_{(1-x)}\text{O}$ is tabulated in Table-1.

Sample	Peak position ($^\circ$)	Plane	β	Crystallite size (nm)
ZnO	36.45	(101)	0.4295	20.33
$\text{Mn}_{0.05}\text{Zn}_{0.95}\text{O}$	36.83		0.4100	19.48
$\text{Mn}_{0.10}\text{Zn}_{0.90}\text{O}$	36.02		0.5050	15.58
$\text{Mn}_{0.15}\text{Zn}_{0.85}\text{O}$	36.63		0.7300	10.94

From the data, it is clear that the crystallite size decreases with the increase of doping concentration since the ionic radius of Mn^{2+} ($0.66 \text{ \AA}$) is smaller than that of Zn^{2+} ($0.74 \text{ \AA}$) [21]. Therefore, such a variation in crystallite size is to be anticipated because of the replacement of Zn^{2+} with Mn^{2+} in the lattice. Steady increase of doping concentration of Mn progressively reduces the concentration of Zn in $\text{Mn}_x\text{Zn}_{(1-x)}\text{O}$. The variation in size reduction can be clarified as follows. The decrease in crystallite size as a function of Mn content can be explained by Zener pinning [34]. There are a variety of inherent defects present in ZnO with different ionization energies such as oxygen vacancy (V_o), zinc vacancy (V_{zn}), oxygen interstitials (O_i) and zinc interstitials (Zn_i) [15]. Due to these crystal defects, the enlargement of grain boundaries becomes limited in a crystal which is called as Zener pinning effect. In the present work, after doping, the number of V_o in the ZnO lattice may be increased. These V_o may limit the development of the crystallites on account of the Zener pinning effect. Fig. 3 shows the calculated crystallite size as a function of doping concentration in $\text{Mn}_x\text{Zn}_{(1-x)}\text{O}$, for $x = 0, 5, 10$ and 15% molar concentrations.

Fig. 3. Calculated crystalline size as a function of Mn doping concentration

The lattice parameters of the synthesized $\text{Mn}_x\text{Zn}_{(1-x)}\text{O}$ samples are also calculated and are tabulated in the Table-2. The lattice parameters are well in agreement with the standard values for 'a' and 'c' with reference to JCPDS card no. 36-1451.

Sample	Lattice parameter (Å)		Volume (Å ³)
	a	c	
ZnO	3.2729	5.3446	49.5801
$\text{Mn}_{0.05}\text{Zn}_{0.95}\text{O}$	3.1640	5.1616	44.6225
$\text{Mn}_{0.10}\text{Zn}_{0.90}\text{O}$	3.1525	5.1232	43.9968
$\text{Mn}_{0.15}\text{Zn}_{0.85}\text{O}$	3.1411	5.1716	44.1448

UV-visible optical characterization: The room temperature optical measurements were performed using a UV-visible-near infrared spectrophotometer. Absorbance spectra of $\text{Mn}_x\text{Zn}_{(1-x)}\text{O}$ nanoparticles are shown in the Fig. 4 and the deviation of the absorbed wavelength with increase in doping

Fig. 4. Absorbance spectra of ZnO and Mn doped ZnO samples

concentration indicates the variation of E_g . In the absorption spectra, a blue-shift (wavelength-decrease) can be seen along with increase in doping concentration. The blue-shift in the E_g is due to the substitution of Zn^{2+} ions in the ZnO lattice by Mn^{2+} ions. In addition to this, the shift in the band gap energy with increase in the doping concentration of Mn can be attributed to the energy difference among the top of the valence band and the vacant energy states in the conduction band [16,35].

The E_g for the ZnO and $\text{Mn}_x\text{Zn}_{(1-x)}\text{O}$ was calculated using the relation $(\alpha h\nu) = \sqrt{(h\nu - E_g)}$, where α is the absorbance and $h\nu$ is the photon energy. To estimate the E_g , $(\alpha h\nu)$ versus $h\nu$ plot was constructed [Fig. 5(a-d)]. The value of E_g was evaluated taking the intercept of the extrapolation to zero absorption with axis, i.e. tends to zero. The approximate E_g value of the ZnO is 3.25 eV which is slightly lower compared to standard value of 3.37 eV [15].

The calculated values of E_g are presented in Table-3. The E_g of the samples increased linearly from 3.25 to 3.68 eV. The increase in E_g with the increase in doping concentration might be ascribed to the alteration of electronic arrangement on doping of Mn ions into the ZnO lattice.

Sample	Energy gap (eV)
ZnO	~ 3.25
$\text{Mn}_{0.05}\text{Zn}_{0.95}\text{O}$	~ 3.60
$\text{Mn}_{0.10}\text{Zn}_{0.90}\text{O}$	~ 3.65
$\text{Mn}_{0.15}\text{Zn}_{0.85}\text{O}$	~ 3.68

There are many calculations and measurements showing that the band gap of pure ZnO depends on the technique of preparation which affects both the oxygen stoichiometry and the grain size. However, it has recently been reported that the E_g can vary between 3.13 eV and 4.06 eV for films deposited by metal-organic chemical vapour deposition (MOCVD) [36]. Fukumura *et al.* [37] and Jung *et al.* [38] examined the blue-shift in E_g with increase in concentration of Mn in thin films of Mn@ZnO. The conclusion of Fukumura *et al.* [37] reveals that an initial decrease of E_g for small concentrations of Mn (< 3 mol %) followed by an increase of E_g for higher doping concentrations of Mn (> 3 mol %) in the mixed samples MnZnO so long as it remains in the wurtzite structure. This type of discrepancy of non-linear variation of band gap is more prominent in the study of Mn-doped ZnO nanocrystals reported by Viswanatha *et al.* [16]. This phenomenon is predicted on the basis of virtual crystal approximation (VCA) because of the higher band gap of MnO, nearly 4.2 eV [26,39]. The E_g of $\text{Mn}_x\text{Zn}_{(1-x)}\text{O}$ samples prepared during the course of this investigation is increased from 3.25 eV, when $x = 0$, to 3.60, 3.65 and 3.68 eV, when $x = 0.05, 0.10$ and 0.15 , respectively, indicating that the Mn is incorporated in ZnO as expected.

Photo catalysis

Photocatalytic degradation of Cr(VI): The reduction of Cr(VI) to Cr(III) was studied to evaluate the photocatalytic activity of $\text{Mn}_x\text{Zn}_{(1-x)}\text{O}$ samples. The optical absorption of

Fig. 5. Optical absorbance spectra of (a) ZnO, (b) $\text{Mn}_{0.05}\text{Zn}_{0.95}\text{O}$, (c) $\text{Mn}_{0.10}\text{Zn}_{0.90}\text{O}$ and (d) $\text{Mn}_{0.15}\text{Zn}_{0.85}\text{O}$ as a function of photon energy

Cr(VI) solution was measured using UV/visible spectrophotometer to understand the photocatalytic degradation of Cr(VI). The degradation of Cr(VI) was investigated with UV light irradiation of both undoped and doped samples under the same ambient conditions. Upon irradiation with UV light, the electrons jump from valence band (VB) to conduction band (CB) creating holes in valence band. The reduction potential for Cr(VI) to Cr(III) with respect to standard hydrogen electrode is 1.33 V [20]. If the chosen catalytic material's conduction band edge is above 1.33 V, the electron, which is in the conduction band, may photocatalytically reduce Cr(VI) to Cr(III) [20].

Photocatalytic activity of $\text{Mn}_x\text{Zn}_{(1-x)}\text{O}$: In the present work, the photocatalytic activity of pure ZnO and Mn doped ZnO was studied for the degradation of Cr(VI) to Cr(III). The reaction pathway for the reduction of Cr(VI) in the presence of $\text{Mn}_x\text{Zn}_{(1-x)}\text{O}$ photocatalyst follows. To carry out the experiment, each time 100 mL of 50 ppm Cr(VI) solution was taken with 10 mM oxalic acid as the hole scavenger and into it 30 mg of the prepared sample was added. This was kept for UV treatment in dark. This sample was studied in different time interval to get a clear idea about the reduction of the toxic Cr(VI) to Cr(III). Diphenyl carbazide (DPC) was used as the indicator. The residual Cr(VI) concentration was determined by UV-visible spectrophotometer

at 540 nm after complexation with DPC. Figs. 6-8 represent the depicts of the normalized concentrations of Cr solution as a function of UV irradiation time over the as-prepared $\text{Mn}_x\text{Zn}_{(1-x)}\text{O}$

Fig. 6. Reduction of Cr(VI) with prepared ZnO

Fig. 7. Reduction of Cr(VI) with 5 % of Mn doped ZnO

Fig. 8. Reduction of Cr(VI) with 10 % of Mn doped ZnO

nanoparticles. In comparison with slow degradation process of Cr, under UV irradiation, with undoped ZnO nanoparticles, the Mn doped ZnO nanoparticles noticeably accelerated the reduction of Cr and the efficiency increases with increase of Mn concentration.

The result from the photocatalytic study shows that pure ZnO as the catalyst took 180 min for the reduction of Cr(III), where the intensity of the peak is reduced and the absorbance reached almost zero. When $\text{Mn}_{0.05}\text{Zn}_{0.95}\text{O}$ was used as the photocatalytic agent for reducing Cr(VI), the time taken for the reduction into Cr(III) is less than what is required with pure ZnO. The reaction gets completed roughly by 150 min, where the intensity of the absorbance peak almost comes to zero. On the other hand, when $\text{Mn}_{0.10}\text{Zn}_{0.90}\text{O}$ used as the photocatalytic agent, the time required for the complete reduction of Cr(VI) to Cr(III) is about 90 min. With $\text{Mn}_{0.15}\text{Zn}_{0.85}\text{O}$, the intensity of the peak, corresponding to the complex of Cr(VI)

with 1,5-diphenyl carbazide, completely get reduced within 60 min. The inference made from this observation is that the time taken for photocatalytic reduction decreases with increase in doping concentration, which was again confirmed by observing the photocatalytic activity under constant time for different dopant concentration.

Effect of doping on photo catalysis: To study the dependence of photo catalysis on doping concentration, a plot has been made (Fig. 9) where we observe the photocatalytic activity under constant time (30 min) for different Mn concentration. As dopant concentration increases, more vacancies are produced in the crystal lattice [30]. These vacancies can increase the number of electrons in conduction band by effectively separating hole-electron pairs with the help of hole scavenger like oxalic acid. Increase in doping concentration can generate more and more free electrons for conduction. These electrons, after getting excited from the valence band to the conduction band, make the reduction faster. Thus, we can account for the reduction in time with increasing doping concentration.

Fig. 9. Reduction of Cr(VI) in 30 min for various Mn concentration

Also, as and when the doping concentration is increased, more and more complimentary electrons will be created for conduction. These electrons, after getting excited from valence band to conduction band, undergo secondary reactions with the free radicals ($\cdot\text{OH}$), which makes the reduction faster [13,40].

Conclusion

The work presented here has been focused on the studies on structural, optical and photocatalytic properties of ZnO and Mn doped ZnO nanoparticles, synthesized by chemical co-precipitation method. We noticed the E_g of the ZnO nanoparticles varies with Mn doping. Also we observed that photocatalytic reduction time reduces with increasing doping concentration. The $\text{Mn}_x\text{Zn}_{(1-x)}\text{O}$ nanoparticles has been observed as an excellent photo catalyst and it showed promising result for the degradation of Cr(VI).

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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