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Article

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Mn-doped ZnO: Role of morphological evolution on enhanced photocatalytic performance

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Abstract

Recently, zinc oxide (ZnO) has attracted much interest, owing to its efficient photocatalytic applications. Herein, we report the synthesis of pristine and Mn-doped ZnO photocatalyst with different nanostructures. The samples were synthesized via simple and low cost co-precipitation method. The synthesized samples were characterized using X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), energy-dispersive X-ray (EDX) spectroscopy, UV–visible diffuse reflectance spectroscopy (UV–DRS) and photoluminescence (PL) studies. The structural analyses revealed the formation of well crystalline nano photocatalyst. Interestingly, doping has altered the morphology of the pristine ZnO significantly from the randomly oriented flakes like structure to rice like structures. The doping of Mn has been established via EDX analyses. Incorporation of Mn has enhanced the photon absorption towards visible region along with the formation of some favorable defect states. The photocatalytic performance of Mn doped ZnO showed superior activity than the pristine ZnO. The enhanced photocatalytic performance of the doped sample can be ascribed to the presence of Mn into the ZnO lattice. Furthermore, doping results into the formation of inter band states which make the easy transfer of excited electrons from the valence band to the conduction band along with efficient electron–hole pair separation. Moreover, the morphological evolution of ZnO due to the doping may also play a vital role in enhancing the photocatalytic performance of the doped sample.

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Keywords: Photocatalysis; Zinc oxide; Doping; Nanostructure; Rate constant; Photonic efficiency

1. Introduction

In past few decades, considerable efforts have been devoted to overcome the energy and environmental issues through the utilization of renewable energy resources. Solar energy utilization has attracted continuous research interest considering the high number of exceptional outcomes in the field of environmental applications [1,2]. Among various strategies, heterogeneous photocatalysis is one of the most promising ways to address energy and

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environmental issues in a most green way. The development of highly efficient photocatalyst for environmental applications has become a commanding task. Among various reported metal oxides, Zinc Oxide (ZnO) is one of the most studied photocatalyst due to its chemical stability, photo-stability, availability and low cost etc. Wang et al. [3,4]. Although ZnO has made its mark during the past few decades, there are still some unsolved limitations which restrict its application in large scale. Poor solar absorption limited to UV region and fast charge carrier recombination results in low photocatalytic performance of ZnO Bora et al. [5]. Among different approaches, doping with semiconductor is an effective way to boost the absorption towards visible region and enhance the lifetime of photo-induced charge carriers [6]. Doping of metal oxide photocatalyst with cations creates local energy states inside the inter band gap of the semiconductor, with shift in the band edge position lying in the visible spectral range [7]. Moreover, the preliminary results available in the literature promise and suggest the need of further exploration of Mn doped ZnO photocatalysis [8].

Present work report the synthesis of Mn doped ZnO photocatalyst through a simple and low-cost co-precipitation method. Structural, morphological and optical properties of pristine and doped samples were evaluated followed by the photocatalytic studies using methylene blue (MB) as probe pollutant.

2. Experimental

Simple co-precipitation method was adopted for the synthesis of pristine and Mn doped ZnO photocatalyst. Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), sodium hydroxide (NaOH) and Manganese (II) sulphate $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ were used as the precursor. Appropriate amount of Zinc nitrate and Manganese (II) sulphate were dissolved in 100 ml distilled water and stirred for 10 min. Aqueous NaOH solution (1M) was added drop-wise to the solution over a period of 15 min to make $\text{pH} = 10$ which results in the formation of a white gelatinous precipitate. The as-formed precipitate was filtered, washed with distilled water and ethanol for many times and dried in oven at $150\text{ }^\circ\text{C}$ for 12 h. In order to further improve the crystallinity, the samples were calcined at $400\text{ }^\circ\text{C}$ for 1 h in muffle furnace. Same procedure was adopted for the comparison with pristine ZnO without addition of Manganese (II) sulphate.

2.1. Characterization

X-ray diffractometer (Proto Model: AXRD Bench top, Canada) was used to carry out the structural analyses of the samples. While, the morphological studies were carried out using Field Emission Scanning Electron Microscopy (FESEM) Nova Nano FE-SEM 450 (FEI) operated at 1 kV (TLD-SE) & 1 nm at 15 kV (TLD-SE). The elemental analyses were scrutinized based on EDS spectra. The spectral response and the defect states were identified using UV–NIR spectrometer with diffuse reflectance attachment (Shimadzu| Model:UV 3600 plus| Origin:Japan) and photoluminescence (PL) measurements (Fluoromax4, Horibe, USA) respectively.

2.2. Photocatalytic degradation experiments

The photocatalytic performance of the samples for the degradation of Methylene Blue (MB) was performed at room temperature under visible light irradiation. The catalyst loading and the dye concentration was kept at 0.5 g/l and 0.015 mM (60 ml) respectively under stirred condition. The solution was initially stored in the dark for 1 h to attain adsorption desorption equilibrium and then exposed to the light. Samples were taken out after specific irradiation time and analysis was carried out using UV–visible spectrophotometer (Agilent Technologies Cary 60 UV–Vis, India) at 663 nm.

3. Result and discussion

Fig. 1 depicts the XRD spectra of the pristine and Mn-doped ZnO samples. The sharp and intense peaks specify the high crystalline nature of the samples. The diffraction peaks were identified and indexed with the help of JCPDS file no. 36–1451 which reveals the presence of wurtzite phase of ZnO. Moreover, no additional peaks were observed indicating the purity of the sample without altering the overall structure of the crystallographic system. The average crystallite size has been estimated using Debye–Scherrer equation and the values of doped sample is found to be increased from 15.04 nm to 19.33 nm [9].

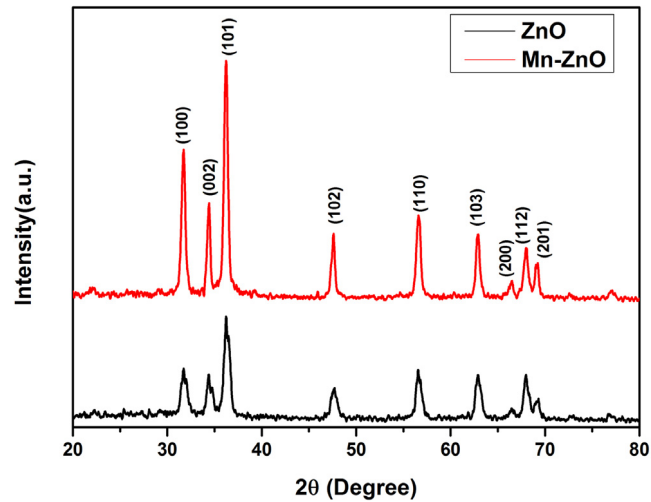


Fig. 1. XRD spectra of the samples.

A high-magnification field emission scanning electron microscopy (FESEM) images were recorded (Fig. 2) to evaluate the surface morphology of the samples. It is clear from the micrographs that both pristine and doped ZnO exhibit two different morphologies. Pristine ZnO shows agglomerated flakes like structure whereas, Mn–ZnO shows the formation of rice grain like structure indicating the evolution in surface morphology due to the doping. Moreover, the doping of Mn inside ZnO matrices is confirmed using EDS analysis and the values are in accordance with experimental data.

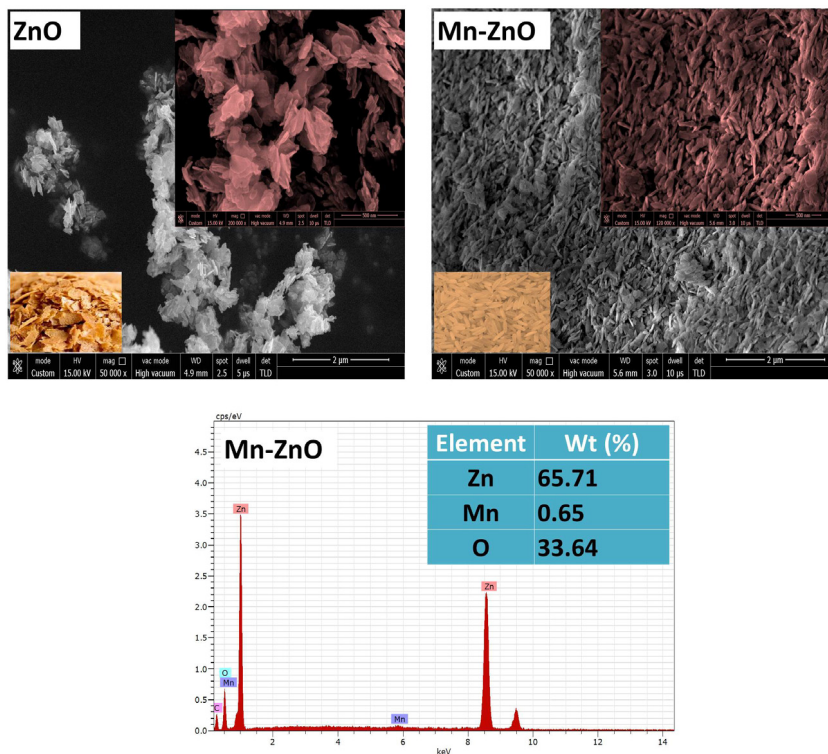


Fig. 2. FESEM and EDS images of the samples.

The optical absorption spectra of the pristine and doped ZnO were recorded and the band gap energy values were calculated using Tauc's plot (Fig. 3(a)) [10]. The spectrum shows a red shift in absorption towards visible region with incorporation of Mn, which is in accordance with FESEM and EDS an analysis. This can be attributed to the formation of inter band states between valence band and conduction band of ZnO after doping [11]. The reduced band gap of the doped ZnO can assist the enhanced absorption of the photon result into higher photocatalytic performance.

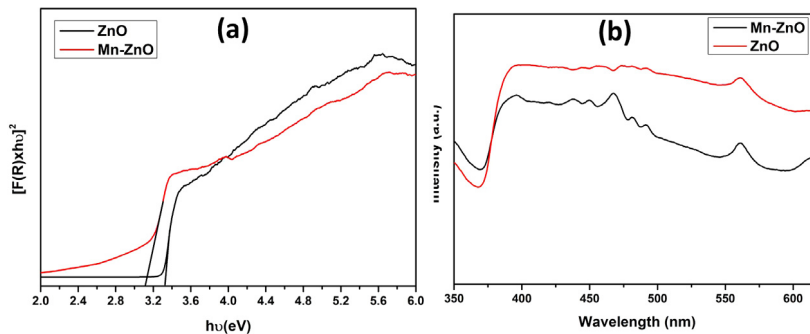


Fig. 3. Tauc's plot (a) and PL spectra (b) of the samples.

The defects states of the samples were identified with the help of PL analyses at an excitation wavelength of 320 nm and shown in Fig. 3(b). The peak centered on 380 nm is due to the near band emission of the samples. The peak ranges from 420 nm to 570 nm can be attributed to the several favorable defect states such as: zinc and oxygen vacancies, zinc interstitials etc. Yu et al. [12]. Moreover, the reduced PL intensity of Mn doped ZnO can be attributed to the lower charge carrier recombination due to the presence of inter band trap levels [13].

The photocatalytic degradation of methylene blue (MB) is investigated for pristine and Mn doped ZnO under visible light (Pro-Light, 100 Watt) irradiation. The degradation spectra and the rate constant spectra of the samples are shown in Fig. 4(a&b). As expected from the physico-chemical analyses, Mn doped ZnO exhibit better photocatalytic performance compared to the pristine one. The rate constant of the doped sample is found to be increased by two times than the pristine one. The improved visible light driven photocatalytic performance of the sample suggests that the Mn modified ZnO leads to the higher photon absorption and defect concentration which contributes significantly to improve the charge separation and, therefore, exhibit enhanced photocatalytic performance.

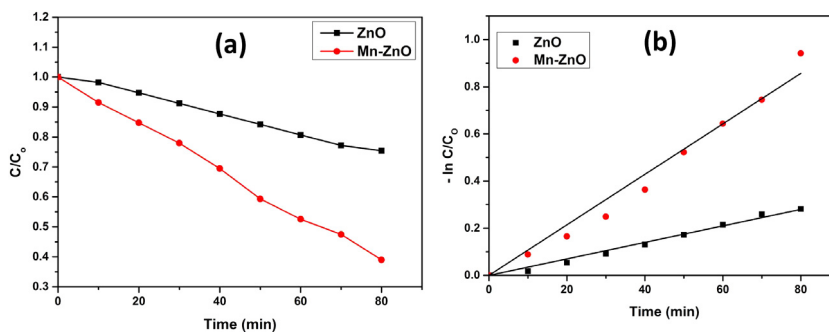


Fig. 4. (a) Degradation kinetics of MB (b) linear fitting of photocatalytic performance.

4. Conclusion

In summary, pristine and Mn doped ZnO samples sequentially prepared by co-precipitation method. XRD analyses confirmed the formation of highly crystalline wurtzite hexagonal ZnO structure. The surface morphology of the sample revealed the evolution of rice grain like structure from the flakes like structure. The evolution of the surface morphology is seems to be favorable for the enhanced photocatalytic performance of the doped samples.

Moreover, the optical analyses confirm the elevated photon absorption towards visible region due to the Mn doping along with the suitable tuning of defect states attribute to the reduced charge carrier recombination. As expected, the superior photocatalytic performance of doped ZnO indicates the strong correlation between physico-chemical properties and the photocatalytic performance.

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