Development of oxygen vacancies and surface defects in Mn-doped ZnO nanoflowers for enhancing visible light photocatalytic activity

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Abstract

Pure and Mn-doped ZnO nanoflowers were successfully synthesized by the hydrothermal technique. Doping of Mn into ZnO lattice exhibits formation of oxygen vacancies and surface modifications into ZnO lattice was investigated by XPS spectra and AFM analysis. During the photocatalytic performance, vacancies create the trap centers for photogenerated electrons hence the electron–hole recombination is effectively inhibited. These formed oxygen vacancies along with enhanced surface area are due to Mn doping, resulted in effective photodegradation of methylene blue solution under solar light irradiation. The degradation efficiency for methylene blue dye exceeds 82% after 120 min under solar light irradiation, also the catalytic performance of Mn-doped ZnO nanoflowers retains even after 4 cycles.

Keywords ZnO nanoflowers · Oxygen vacancies · Photocatalytic degradation · Surface defects

1 Introduction

At present zinc oxide (ZnO) is the most promising semiconductor material which has been studied extensively in the last few decades for distinct applications such as photocatalysis, optics, electronics, semiconductor materials, piezoelectric, magnetic and biomedicine due to its multifunctional nature and properties. ZnO nanomaterials have fascinated great attention owing to their low cost, ease to fabrication of various nanostructured materials, chemical and thermal stability, photocatalytic activities, and wide band gap semiconductor, unique optical, electrical, structural and physical properties. One-dimensional (1D) semiconductor nanomaterials such as nanowires, nanorods, nanobelts, and nanoflowers have been used for technology and industrial applications. In today's research on photocatalytic activity, these nanostructures are most significant nanomaterials due to their high surface to volume ratio and smaller band gap [1–3]. To enhance the

photocatalytic activities, the following parameters affect photocatalytic efficiencies such as a surface area to volume ratio, porosity, oxygen vacancy, surface defects, conductivity, thermal stability, chemical stability, high mobility and low band gap [4–6]. Recently ZnO is strong semiconducting nanomaterial for degradation of methylene blue, methyl orange, rhodamine-B, and congo red, etc. organic dyes and purification of water owing to its high reactivity, environment-friendly nature, non-toxic and cost-effective. Therefore, researchers are interested to achieve aforesaid parameters and synthesized ZnO nanomaterials by diverse methods such as metal–nonmetal doping, surface modification via organic materials, combining semiconductor oxide nanoparticles with conducting polymers, irradiation source, pH, addition of carboxylic compounds, distinct composites with ZnO/TiO₂/GO, using various surfactant for different morphology (template method), etc. to degrade highly toxic dyes [7–11].

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However, the disadvantage of ZnO nanomaterials is due to its large band gap of 3.37 eV, therefore, it absorbs light only in the UV region that is only about 5% of the solar spectrum and it is the challenge for researchers. Therefore, the effective use of solar energy still remains a challenge in photocatalytic applications. Due to this problem, we have introduced solar radiation to study the degradation of methylene blue using ZnO thin film. To improve the photocatalytic activity of ZnO in visible radiation, it is necessary to either reduce its band gap or introduce intermediate donor levels with the doping of transition metals. In our preceding publication, we have reported work on nanorods [12] but in the present work, we have prepared nanoflowers because they are highly reactive than nanorods due to their high surface area actively participated in photocatalytic reaction. The doping of transition metals namely Mn, Ni, Ag, Cu, Co, La, Ce, Au, etc. in ZnO lattice helps the growth of one-dimensional single-crystalline nanostructure on the glass substrate and also reduces the band gap of semiconductor material. Furthermore this doping into the ZnO lattice introduces point defects viz. oxygen and zinc vacancies thereby inducing intermediate bands in the forbidden bandgap of ZnO [13–16] These interesting changes in properties of Mn-doped ZnO have their own importance in research fields, promoting to study the photocatalytic activity of Mn-doped ZnO nanocrystals [17].

There are many methods are available for the synthesis of ZnO nanoflowers such as dip coating technique [18], sol–gel and spin coating [19], chemical bath deposition [20], chemical vapor deposition [21], hydrothermal [22]. We have selected the hydrothermal technique to synthesis Mn-doped ZnO nanoflowers because it is a cost-effective and most appropriate technique for getting fine morphology of one-dimensional single crystalline material. To study the effect of photocatalytic activity of pure and Mn-doped ZnO nanoflowers under solar light may change optical, electrical and morphological properties of ZnO because their atomic radii are almost equal and properties are influenced by the quantum confinement of electronic states of bulk ZnO are due to doping of transition metals [23]. Here, we report our work on the development of oxygen vacancies and surface defects into pure and Mn-doped ZnO nanoflowers in an effective approach. All samples of pure and Mn-doped ZnO nanoflowers exhibit high photocatalytic activity and good stability during the photocatalytic performance. We have further investigated the crystal structure, grain size, morphology of the as-prepared Mn-doped ZnO samples by X-ray diffraction and surface elemental composition and surface state by XPS spectroscopy.

2 Experimental details

2.1 Material synthesis

Pure and Mn-doped ZnO nanoflower thin films were grown on a glass substrate by hydrothermal technique successfully. For the synthesis of Mn-doped ZnO, 1 M Zinc acetate dihydrate, 0.04 M manganese chloride and 1 M of Hexamethylenetetramine (HMTA) were dissolved separately in distilled water. The HMTA solution was added in Zinc solution and dropwise ammonia was added to clear the precipitate (pH ~ 10) and stirred this solution for 2 h. For the deposition of thin films firstly ultrasonicated the glass substrate using HCl in an ultrasonic cleaner for 2 h. The substrate was dried and kept aligned in Teflon lined stainless steel autoclave (100 ml capacity) after that above solution was transferred into the autoclave. Sealed the autoclave and kept in a muffle furnace at 70 °C for 6 h. Deposited films were cooled followed by room temperature and then washed with distilled water. After washing, deposited films were dried at room temperature. Samples were dehydrated and demineralized at 110 °C for 3 h in HAMCO tubular furnace. The same synthesis procedure was used for the preparation of pure ZnO samples.

2.2 Dye degradation activity

The photocatalytic performance of pure and 4% Mn-doped ZnO thin films were examined by the photocatalytic decomposition of Methylene Blue (MB) in an aqueous suspension under solar light irradiation. In a typical experiment (1×1) cm² of pure and 4% Mn-doped ZnO catalyst film was suspended in 0.5 mg MB in 100 ml deionized water solution. The catalytic thin-film suspension was stirred for 10 min in dark and then the system was exposed under solar light irradiation with continuous stirring using a magnetic stirrer. Solar light irradiation was carried out from 12 p.m. to 3 p.m. during the winter season in Aurangabad, Maharashtra, India. The latitude and longitude are 19.85°N and 75.35°E respectively. The average sunlight intensity was found to be around 600 W/m². To compare the photocatalytic activity of both pure and Mn-doped ZnO catalysts, the experiment was conducted simultaneously to avoid errors arising due to fluctuations in solar intensity. The solution was collected for 20 min of time intervals and analyzed by UV–visible spectroscopy. Also for further comparison the photocatalytic degradation of 4-nitrophenol was studied (ESI).

2.3 Material characterizations

The structural parameters were investigated by XRD using D-8 advanced diffractometer (Bruker AXS, Germany) with

a monochromatic CuK_α radiation source with wavelength ($\lambda = 1.54 \text{ \AA}$) and scintillator detector at a scanning rate of 1° per minute. The effective concentration and binding-state of the ions in the pure and Mn-doped ZnO samples were characterized by X-ray photoelectron spectroscopy (XPS) (ESCA-LAB 250 Xi, Thermo-VG Scientific). Defect states and fluorescence properties of pure and Mn-doped ZnO samples were demonstrated using the UV-Vis spectrometer with an LED lamp (Avantes Spec-ULSi2048L-USB2). The surface morphology of as-prepared samples was verified by scanning electron microscopy (SEM) with resolution $5\text{--}10 \mu\text{m}$. The absorption spectrum and energy band gap was measured using a UV-Vis spectrometer (Avantes Spec-ULSi2048L-USB2).

3 Results and discussion

3.1 Structure parameters

Lattice parameters, crystal size, lattice strain, the volume of the unit cell and c/a ratio of the $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ with $x=0.00$ and 0.04 nanoflowers were examined using X-ray diffraction patterns along with Rietveld refinement technique. It was found that after doping of Mn into ZnO lattice, the aspect ratio of the diffraction peaks were increased along planes (100) (002). This observation proposes on doping

of Mn into ZnO lattice enhances lattice crystallinity. Lattice parameters were attained from the Rietveld Refinement technique summarized in Table 1. The slight change in lattice parameters after 4% Mn doping into ZnO lattice was noted due to Mn ions which have smaller ionic radii ($0.66 \text{ \AA}$) than Zn ions ($0.74 \text{ \AA}$), it means a however small amount of Mn may change physical properties of ZnO material. Distortions may be developed in Mn-doped ZnO lattice owing to the approximately same ionic radii which reflects the change in lattice parameters in the system [24]. The average crystallite size of pure and Mn-doped ZnO samples was verified by employing the following formula [25].

$$D = \frac{C\lambda}{\beta \cos \theta} \quad (1)$$

All sharp XRD peaks were indexed by the hexagonal wurtzite phase of ZnO (JCPDS Card No. 96-900-4180) as shown in Fig. 1. It is explicitly corroborated sharp peaks exhibit the as-synthesized material is in good crystallinity state in the form of hexagon nanoparticles and Mn-doped ZnO in the form of nanoflowers. In pure ZnO the ratio of the intensity of peak along (100), (002) and (101) planes is lower than 4% Mn-doped ZnO nanoflowers were observed nanoparticles without growth in (002) plane but which enhances for 4% Mn-doped

Table 1 Lattice parameters, crystal size, lattice strain, volume of the unit cell, u parameter and c/a ratio of pure and Mn-doped ZnO nanoflowers

Sample	Lattice parameter		Scherrer's method D (nm)	W-H method		The volume of the unit cell ($\text{\AA}^3$)	u parameter	c/a ratio
	a (nm)	c (nm)		D (nm)	$\epsilon \times 10^{-4}$			
Pure ZnO	0.3250	0.5206	27.1946	30.94955	8.29	47.6240	0.379898	1.6019
4% Mn:ZnO	0.3251	0.5209	27.2145	33.33029	12.0	47.7114	0.379861	1.6021

Fig. 1 Rietveld refinement of **a** pure ZnO and **b** 4% Mn-doped ZnO nanoflowers

ZnO sample indicating the growth of the single crystal. It may be owing to Mn which functions as a metal catalyst and assists in the growth of nanoflowers outlines the doping effect of Mn into ZnO host lattice [26]. Using Debye–Scherrer's and Williamson–Hall methods crystalline size and effect of strain were evaluated for the pure and Mn-doped ZnO nanoflowers [27]. The variation of $\beta \cos \theta$ with $4 \sin \theta$ gives the Williamson–Hall plots from which the crystallite size D and lattice strain ϵ are shown in Fig. 2. W–H method results that the crystallite size enhances with the doping of Mn in ZnO lattice. This is due to the Mn doping which has a smaller ionic radius that causes bigger strain in the lattice. The positive strain implies an expansion in the system due to this doped system shows higher crystallite size values which were calculated by W–H method as compared to the crystallite size calculated by Scherrer's method [27, 28]. The volume of unit cell enhances for Mn doping due to the positive strain that produces expansion in the lattice system. Using the following formula, the internal parameter u was calculated.

$$u = \frac{a^2}{3c^2} + 0.25 \quad (2)$$

where u is an internal parameter, a and c are lattice constants. From Eq. (2) one confirms that there is a strong correlation between the c/a ratio and ' u '. It was acknowledged that the internal parameter ' u ' decreases with increasing c/a ratio in such a way that those four tetrahedral distances remain nearly constant through a distortion of tetrahedral angles due to the long-range polar interaction [29].

The aspect ratio of (100) and (002) peaks was observed from XRD patterns which exhibit a higher aspect ratio than pure for 4% Mn-doped ZnO sample.

More importantly, the hydrothermal method is a successful and general procedure to control the aspect ratio and adjust the surface defects. The high aspect ratio and Crystallinity of 4% Mn-doped ZnO nanoflowers are playing major and responsible role for the higher photocatalytic activity under solar light irradiation.

3.2 X-ray photoelectron spectroscopy

For the demonstration of the photocatalytic mechanism that involves Mn^{2+} doping and vacancy defects on the nanoflowers surface, the surface element compositions and chemical phases of both pure and 4% Mn-doped ZnO samples using XPS analysis outlined. From XPS analysis, the presence of Zn and O elements are observed in both samples as shown in Fig. 3, but the existence of Mn is only in the Mn-doped ZnO sample. For the conformation of chemical phases of each element, high-resolution XPS spectra for Mn 2p, Zn 2p, and O 1s states are depicted in Fig. 4a–d. For a 4% Mn-doped ZnO sample, double peaks at 641 and 651 eV corresponded to the Mn^{2+} 2p level of $P_{3/2}$ and $P_{1/2}$, respectively, indicating that the chemical state of Mn has existed as Mn^{2+} in 4% Mn-doped ZnO samples. It was explicitly confirmed that the Mn^{2+} doped ZnO sample was successfully prepared. In Fig. 4b, the peaks related to Zn 2p for both samples are observed and there are two symmetric peaks present in the Zn 2p region. The peak centered at 1022 eV corresponds to Zn $2p_{3/2}$ and another one centered at 1045 is assigned to Zn $2p_{1/2}$, indicating a normal state of Zn^{2+} in the both samples. From Fig. 4c, d it is clearly seen that the high-resolution O 1s spectra for pure and Mn-doped ZnO samples respectively. It reflects the asymmetric O 1s core spectrum deconvoluted with one and three peaks respectively. In the case of pure ZnO sample, only one peak at 531.5 eV which was assigned to

Fig. 2 Plots of W–H method for $4 \sin \theta$ versus $\beta \cos \theta$ of Pure and 4% Mn, doped ZnO nanoflowers

Fig. 3 Full scan XPS spectra of pure and Mn-doped ZnO nanoflowers

O^{2-} ions in the oxygen-deficient regions and is related to oxygen vacancies [30]. In the Mn-doped ZnO sample, the first peak centered at 529.9 eV corresponds to the O^{2-} ions in the wurtzite structure (O–Zn). While the medium peak at 531.5 eV is assigned to O^{2-} ions in the oxygen-deficient regions. The FWHM of O 1s peak for pure ZnO was 2.70 and for 4% Mn-doped ZnO, it was decreased up to 2.40. It was exhibited that the O 1s peaks for Mn-doped ZnO nanoflowers become slightly smaller with increasing of surface defects or large surface area. It was fitted by Gaussian distribution with two peaks which corresponded to O–Zn and O–H respectively. The medium binding energy component, centered at 531.5 eV, was due to the variations in the concentration of oxygen vacancies; therefore, the intensity change is due to the variations in the concentration of surface oxygen vacancies. The intensity of this peak increases after substituting Mn^{2+} in ZnO [31]. Peak intensity was found to increase for 4% Mn-doped ZnO sample exhibits its diffusion of atoms towards the surface. The increase in surface defects and variation in surface oxygen vacancies are helpful to increase the photocatalytic activity of

Fig. 4 **a** Mn 2p spectra, **b** Zn 2p, **c** O 1s of pure ZnO and **d** O 1s of 4% Mn-doped ZnO nanoflowers

photocatalyst. Surface defects play a very important role in the photocatalytic activity hence the 4% Mn-doped ZnO nanoflowers with high aspect ratio and surface defects is responsible for the higher photocatalytic activity under visible light irradiation. In reported literature, XPS results show that the formation of oxygen vacancies after annealing treatment while in our study Mn-doped ZnO sample exhibits the formation of oxygen vacancies at room temperature which indicates that Mn is responsible for the formation of oxygen vacancies [32].

3.3 Scanning electron microscopy

Morphological variations for Mn-doped ZnO nanoflowers were observed using the SEM technique. Figure 5 shows the images of pure and Mn-doped ZnO nanoflowers consisting of nanorods, which were hydrothermally grown on the glass substrates without the ZnO seed layer. In pure ZnO sample, hexagonal nanoparticles with a flat surface were observed but for 4% Mn-doped ZnO sample, nanoflowers were formed. It was outlined from the figure the small-sized nanoflowers with a large number of branches formed in the Mn-doped ZnO sample. Based on the literature of previously reported work and the results of the present work, we have observed that the formation of nanoflowers for a 4% Mn-doped ZnO sample could be achieved in the presence of Mn metal catalyst. In the present work, the formation of Mn-doped ZnO nanoflowers obtained from anisotropic growth under the effects of hydrothermal conditions. Variations in the ionic strength of the hydrothermal solution for Mn may contribute to the formation of nanoflowers. Thus Mn plays a vital role in the formation of the Mn-doped ZnO nanoflowers. In a hydrothermal process, anisotropically grown single crystal along the c-axis to form hexagonal rod which

depends on the concentration of dopant Mn, Zinc solution and HMTA which were used in the synthesis method. However, when the concentration of ZnO and Mn nuclei is more, then they easily aggregate together to decrease surface energy. Every nucleus in the aggregate grows anisotropically along the c-axis, forms an Mn-doped ZnO nanoflowers [33]. The grain size of the pure ZnO sample was calculated and found to be 50 nm. The length and diameter of Mn-doped ZnO nanoflowers were calculated by image-j software which was found to be 652 nm and 94 nm respectively.

3.4 UV–Vis spectroscopy

To determine the optical properties of the pure and Mn-doped ZnO, the absorbance spectra were used. UV–Vis absorption technique was used to examine the change in the energy band structure of ZnO on the substitution of Mn. The room temperature UV–Vis absorption spectra of pure and 4% Mn-doped ZnO nanoflowers in the wavelength range 350–900 nm was investigated and shown in Fig. 6. The sharp absorption edge observed around 380 nm for both samples. The absorption coefficient (α) was intervened, which depends on the film thickness and absorption, by the following equation [34]:

$$\alpha = 2.303A/t \quad (3)$$

where A is the absorbance and t is the thickness of the sample. The energy band gap of the pure and Mn-doped ZnO was calculated by the following Tauc equation [34]:

$$\alpha h\nu = A(h\nu - E_g)^{1/2} \quad (4)$$

where A is the constant, E_g is the energy gap, ν is the frequency of the incident radiation and h is Planck's constant.

Fig. 5 SEM images of **a** pure, **b** 4% Mn-doped ZnO nanoflowers

Fig. 6 UV-Vis absorbance spectra and the band gap of Pure and 4% Mn-doped ZnO nanoflowers

ZnO is a direct band gap semiconductor; the optical band gap was investigated by the plot of $(\alpha h\nu)^2$ versus $h\nu$. The band gap of 4% Mn-doped ZnO is small as compared to the band gap of Pure ZnO which outlines the redshift. This is due to the quantum confinement of electron in one dimensional Mn-doped ZnO nanoflowers [28]. The efficiency of photocatalysis depends upon the harvested region of the solar spectrum by ZnO nanomaterials and the rate of electron-hole pair generation. Due to the wide band gap of ZnO can harvest only in the UV region. For the enhancement of photocatalytic efficiency, it is essential to absorb a larger spectrum of sunlight so that more electron-hole pairs can be generated [35, 36]. For this reason, a narrow band gap is required for the enhancement of photocatalytic efficiency. In our investigation, 4% Mn-doped ZnO nanoflowers have a narrow energy band gap which plays a vital role in photocatalytic activity. The refractive index is one of the most important factors for designing the nanostructured thin film material which enhances photocatalytic efficiency and acts as the function of wavelength to predict the photoelectric behavior. The refractive index (n) of pure and Mn-doped ZnO nanoflower was estimated by using Herve-Vandamme equation [37, 38].

$$(n) = \sqrt{1 + \left(\frac{A}{E_g + B} \right)^2} \quad (5)$$

where $A = 13.6$ eV and $B = 3.4$ eV are the constants, and E_g is the optical energy band gap which was obtained from Tauc's equation, and it was explicitly confirmed the relation was well suited for optical property studies. Standard optical Refractive index value is for ZnO nanomaterial has $n = 2.0034$ reported in the literature but in our as-prepared sample for pure ZnO $n = 2.2682$ and for Mn-doped ZnO

nanoflowers $n = 2.3515$ which demonstrates enhancement in refractive index values after owing to the creation of oxygen vacancy.

3.5 Atomic force microscopy

Analysis of 3D surface topography of pure ZnO and 4% Mn-doped ZnO nanoflowers from atomic force microscopy was examined and found in good agreement with structural and morphological parameters. Root mean square (RMS) roughness of Pure ZnO nanoparticles was obtained to be 260 nm whereas for Mn-doped ZnO nanoflowers it was reduced to 118 nm. Pure ZnO has higher roughness due to non-uniform deposition on a glass substrate [18, 39] and its thickness was also larger than Mn-doped ZnO nanoflowers while Mn-doped ZnO nanoflower thin film deposited uniformly and growth of nanoflowers was also uniformly as depicted in Fig. 7. From histogram as depicted in Fig. 7c is the double exponential distribution which is symmetric distribution but as compared to normal, which has a stronger peak with rapid decay and heavier tails. In Pure ZnO nanoparticle sample, skewness was calculated by theoretically we would expect near zero but experimentally it was found to be -0.3 and kurtosis was 5.77 . From the histogram, as shown in Fig. 7d is the normal distribution which reveals symmetric distribution with well-behaved tails. Mn-doped ZnO nanoflowers have a skewness of -0.08 which means left-skewed distributions and its Kurtosis of 2.80 which was closer to the expected value of 3 [40, 41]. It outlines that, this sample verifies the symmetry belonging to the morphology. From the analysis of roughness, skewness, and Kurtosis it may conclude that the Mn-doped ZnO nanoflower sample is the best candidate for photocatalytic activity application.

3.6 Photocatalytic activity

The photodegradation efficiency of photocatalytic reactions is much dependent on the specific surface area of the photocatalysis. Photocatalytic activity of the pure and Mn-doped ZnO was intervened by monitoring the degradation of Methylene Blue dye solution under visible irradiation in the presence of the catalyst. Absorbance spectra of the dye solution were measured at intervals of 20 min under visible irradiation for pure and 4% Mn-doped ZnO thin films (1×1 cm)² as shown in Fig. 8a, b respectively. The intensity of the characteristic absorption peak of MB was around 642 nm decreased with an increase in irradiation time. For the pure ZnO photocatalyst, the peak was almost disappeared up to 0.08 (a. u.) after 2.6 h irradiation while for the 4% Mn-doped ZnO nanoflowers, this was about 2 h. The photocatalytic degradation efficiency of the pure and 4% Mn-doped ZnO nanoflowers were verified and found which results for pure

Fig. 7 AFM images of **a** pure ZnO, **b** Mn-doped ZnO, and histogram of **c** pure ZnO, **d** Mn-doped ZnO nanoflowers

and 4% Mn-doped ZnO were 65% and 81%, respectively which confirms that Mn-doped ZnO nanoflowers are more efficient in photocatalysis. Kinetic studies were performed for pure and 4% Mn-doped ZnO samples these results are depicted in Fig. 9a, b. It is noted that the photodegradation of methylene blue follows pseudo-first-order kinetics, which is given below [12],

$$\log \frac{C_0}{C_t} = kt \quad (6)$$

where C_0 and C_t are the concentrations of methylene blue at time $t=0$ and time $t=120$ min, respectively, k is the pseudo-first-order rate constant. The rate constant (k) was verified using the slope of the plot of $\log \frac{C_0}{C_t}$ versus irradiation time. The values of rate constant (k) for pure and 4% Mn: ZnO are 0.2209 and 0.3457 respectively which outline that 4% Mn-doped ZnO sample has a higher rate constant than pure ZnO sample, it may be the formation of defects. The enhancement in degradation efficiency and rate constant for 4% Mn-doped ZnO sample can be attributed to

Fig. 8 Time-dependent absorption spectra of MB solutions in the presence of **a** pure ZnO and **b** 4% Mn-doped ZnO nanoflowers

Fig. 9 Plots of **a** C/C_0 and **b** $\log(C_0/C_t)$ for Pure and Mn-doped ZnO nanoflowers

the high surface area, higher crystallinity, reduced rate of electron–hole recombination and oxygen vacancies as compared to pure ZnO sample. It is noticed that ZnO photocatalysis is based on the generation of an electron–hole pair in light irradiation. It was corroborated that the photo-induced electron–hole easily recombined in the photocatalytic activity. Therefore, it is important to reduce the surface recombination of electrons and holes. Oxygen vacancies can act as electron acceptors during the photocatalytic reaction and thus reduce the recombination rate. Therefore, oxygen vacancies can play a vital role to enhance the photocatalytic properties of photocatalyst [42]. During the photocatalytic performance, vacancies and defects create the trap centers of photogenerated electrons hence the electron–hole recombination is effectively inhibited. Oxygen vacancies also act as charge carrier traps as well as adsorption sites where the charge transfers to adsorbed species, which can prevent electron–hole recombination. To evaluate the reusability of pure and Mn-doped ZnO samples photocatalyst, the degradation efficiency of MB under visible irradiation in four cycles as shown in Fig. 10. Over the four cycles degradation efficiency remains the same which indicates the stability of prepared samples. Nur Ajrina et al. reported that photodegradation efficiency for 7% Mn-doped ZnO nanorods was 76.75% under UV irradiation while in our case it was 82% for 4% Mn-doped ZnO nanoflowers under visible irradiation [43]. This clearly verifies that the 4% Mn-doped ZnO nanoflowers on glass substrate are reusable and more stable. Therefore 4% Mn-doped ZnO sample is a promising candidature for photocatalytic degradation under visible light irradiation and functions effectively (Table 2).

Fluorescence spectroscopy and BET surface defect study results were supplied in ESI [12, 44–46].

Fig. 10 Variation of the relative concentration of MB dye solution under visible irradiation in the presence of pure and 4% Mn-doped ZnO nanoflowers over 4 cycles

4 Conclusions

Pure and Mn-doped ZnO nanoflowers were successfully synthesized by the hydrothermal method and also the photocatalytic activity performance intervened in the as-prepared samples successfully. It is explicitly concluded that the obtained 4% Mn-doped ZnO nanocatalyst exhibits an excellent candidate with high photocatalytic performance for the degradation of the methylene blue dye (MB) than pure ZnO catalyst under the solar light irradiation. The produced pure and Mn-doped ZnO catalyst samples were found to depend on the synthesis parameters in their morphology, crystallite size, surface

Table 2 Comparative table for MB dye degradation in sunlight/visible light

Sr. No.	Photo catalyst	Dye concentration	Time (h)	Photo degradation efficiency (%)	Ref. nos.
1	α -Bi ₂ O ₃	2×10^{-5} M	6	30	[47]
2	α -Fe ₂ O ₃	20 mg/L	8.3	51	[48]
3	CuO	3×10^{-5} M	6	43	[49]
4	ZnS:CdS (wt% 50:50)	10 mg/L	6	65	[50]
5	Pure ZnO	5 mg/L	2.6	65	Present work
6	4%Mn:ZnO	5 mg/L	2	81	Present work

area and subsequently photocatalytic activity. The photocatalytic performance of 4% Mn-doped ZnO nanoflowers has a faster rate constant than pure ZnO which indicates Mn is promising candidature for improving the photocatalysis. XPS results show the incorporation of Mn into ZnO lattice. The formation of oxygen vacancies and defects which are important parameters for the improvement in photocatalytic activity. The presence of green emission in fluorescence spectra signifies that more defects are present in 4% Mn-doped ZnO nanoflowers. All characterizations and evaluation tools support that a 4% Mn-doped ZnO sample under solar light irradiation is an excellent catalyst and financially affordable.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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