

Communication

Manganese-Doped Zinc Oxide Nanostructures as Potential Scaffold for Photocatalytic and Fluorescence Sensing Applications

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Abstract: Herein, we report the photocatalytic and fluorescence sensing applications of manganese-doped zinc oxide nanostructures synthesized by a solution combustion technique, using zinc nitrate as an oxidizer and urea as a fuel. The synthesized Mn-doped ZnO nanostructures have been analyzed in terms of their surface morphology, phase composition, elemental analysis, and optical properties with the help of scanning electron microscopy (SEM), X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDS), and UV-Visible (UV-Vis) spectroscopy. A careful observation of the SEM micrograph reveals that the synthesized material was porous and grown in very high density. Due to a well-defined porous structure, the Mn-doped ZnO nanostructures can be used for the detection of ciprofloxacin, which was found to exhibit a significantly low limit of detection (LOD) value i.e., 10.05 μ M. The synthesized Mn-doped ZnO nanostructures have been further analyzed for interfering studies, which reveals that the synthesized sensor material possesses very good selectivity toward ciprofloxacin, as it detects selectively even in the presence of other molecules. The synthesized Mn-doped ZnO nanostructures have been further analyzed for the photodegradation of methyl orange (MO) dye. The experimental results reveal that Mn-doped ZnO behaves as an efficient photocatalyst. The 85% degradation of MO has been achieved in 75 min using 0.15 g of Mn-doped ZnO nanostructures. The observed results clearly confirmed that the synthesized Mn-doped ZnO nanostructures are a potential scaffold for the fabrication of sensitive and robust chemical sensors as well as an efficient photocatalyst.

Keywords: nanostructures; chemical sensor; photocatalytic activity; ciprofloxacin; methyl orange

1. Introduction

Water is the precious component of nature; unfortunately, the negative consequences of modernization have led to the deterioration in the quality of water. Water pollution is caused due to the excessive use of antibiotics, pesticides, domestic waste, and industrial effluents [1–5]. Population explosion and human greed have put pressure on all types of resources; as a result, the demand–supply chain is the worst affected. Increasing population has increased the demand of industrial and agricultural products, which in turn promotes the excessive use of various chemicals, fertilizers, and pesticides, leading to water pollution [6–8]. The contamination of the environment with these hazardous chemicals has tremendously affected the health of living organisms [9,10]. OSHA Permissible Exposure Limits (PELs) are occupational exposure limits issued by the Occupational Safety and Health Administration (OSHA) in the United States. Due to the presence of various types of pollutants, one needs to think about the advance technologies to detect the presence of these chemicals below the OSHA PELs as well as to degrade them [11–13]. Nanotechnologies are expected to be the new generation of emerging innovative technologies of the 21st century. The new technologies have the potential to develop new innovative materials, devices, and systems with wide-ranging applications, providing promise to solve many of the world's modern problems [14–20].

Antibiotics are an important class of chemical that has been widely used to save lives from bacterial infection. Ciprofloxacin, a third-generation synthetic fluoroquinolone antibiotic, is highly active against a broad spectrum of Gram-negative and Gram-positive bacteria. Among various antibiotics, ciprofloxacin in particular treats a number of bacterial diseases such as urinary tract infection, digestive, respiratory tract, pulmonary, and joint infections [21]. The ciprofloxacin enters into the food cycle through a number of routes that are intentional as well as unintentional such as the disposal of surplus drug, poor handling in the hospitals and pharmaceutical companies, and the release of excreta from human and animals [21–23]. Due to these activities, ciprofloxacin is continuously released into the environment. It cannot be metabolized readily, so it proves highly toxic toward the microorganism, retarding aquatic vertebrates [24,25] and also inhibiting the process of photosynthesis [26], which leads to the growth of antibiotic resistance bacteria in the environment [27]. Since the presence of ciprofloxacin in the environment leads to a series of problems, it is highly recommended to design a reliable and robust chemical sensor for its rapid detection.

On the other hand, industrial and domestic effluents contain a variety of organic chemicals that are pollutants, which are required to be treated before being discharged to the environment. Among the organic molecules are colored dyes, which are released in the environment through waste water effluents of various industries such as textile, leather, food, plastics, cosmetics, etc. [28–30]. Particularly, azo dyes are extensively used due to their superior performance, but they are extremely hazardous to the environment. Moreover, most of the organic dyes as pollutants proved potentially carcinogenic [31]. These polluted effluents, when entered into an open environment, are bound to spread aesthetic pollution and disturb the ecosystem. So, in order to save the aquatic life as well as avoid various health issues, such organic molecules must be removed or destroyed from waste water. Since these issues are of immense public concern, the development of new methods with consistent improvement in treating the pollution is essential if new technology is to emerge and alleviate many of the pressing health problems.

The above discussion clearly reveals that antibiotics and organic dye both belong to the class of highly toxic chemicals. So, the detection as well as the degradation of these type of chemicals is the need of analysis. Nanotechnology could have huge potential in the environmental science for the sensing and removal of contaminants and to make the planet safe for living [32–34]. Nanotechnology has a greater possibility to deal with these problems, especially metal oxides (TiO_2 , ZnO , ZnS , CdS and CuO), which are semiconductor materials. Among several metal oxides, TiO_2 is attracting attention due to its efficiency, large band gap, chemical stability, low cost, and non-toxic nature [34–37].

In addition, ZnO shows a wide band gap of 3.37 eV. It is non-toxic, inexpensive, and chemically stable. It is known to possess high radiation hardness, remarkable optical absorption in the UV range,

effective transparency and outstanding thermal properties. ZnO is used in several applications such as photocatalysis, catalysis, antibacterial products, solar cells, medicines, opto-electronics, etc. [38,39]. The immense use of ZnO can be observed in photocatalysts, catalysts, and antibacterial agents, due to its biocompatibility, non-toxic, and excellent redox properties [40,41]. The doping of transition metals (e.g., Co, Mn, Fe, Ni, and Cu) onto ZnO improves its optical and electrical properties [42,43]. Therefore, in the present paper, among the various transition metal ion-doped metal oxides, we have focused on the Mn-doped ZnO nanostructures, as it provides an intermediate energy level, defect states that lead to the decrease in electron-hole recombination, and hence better sensing and photocatalytic properties [44,45]. In other words, the same material can perform a variety of applications. Furthermore, the high solubility of ZnO [46], wide direct band gap energy of 3.37 eV, and large exciton binding energy of 60 meV [47,48] are properties that show improvements due to the large magnetic moment of the Mn atom. The solution combustion synthesis route was utilized in the present paper, as this is a time and energy-saving single-step facile process for the bulk production of nanoparticles [49,50]. The as-synthesized Mn-doped ZnO nanomaterial has been utilized for the fabrication of a luminescence chemical sensor for the detection of ciprofloxacin as well as the degradation of methyl orange as an Azo dye in aqueous medium.

2. Experimental

2.1. Materials

Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), manganese nitrate tetrahydrate ($\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), urea (NH_2CONH_2), and ciprofloxacin are of analytical grade obtained from Sigma-Aldrich. These chemicals were applied directly without any further processing. Milli-DI® Water Purification System for Deionized (DI) water from Merck KGaA, Darmstadt, Germany, was used for all the experiments.

2.2. Synthesis of Mn-Doped ZnO Nanostructures

Manganese-doped zinc oxide nanostructures were synthesized by using a facile one-step solution combustion approach using $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ as an oxidizer and urea (NH_2CONH_2) as a fuel in a stoichiometric ratio ($\varphi = 1$). In the typical synthesis procedure, 4.0 g of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 1.34 g of NH_2CONH_2 were taken in different beakers; then, 50 mL of DI water was added to both the beakers separately. Both solutions were mixed at room temperature (RT) thoroughly with regular stirring for 30 min followed by the dropwise addition of 50 mL of 0.13 M $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ solution. This solution mixture was heated until the excess water content evaporates and the solution turns into a gel-like material. Then, the resultant gel-like material was placed in a muffle furnace maintained at 400 °C for 1 h. This led to combustion of the reaction mixture and the formation of crystalline Mn-doped ZnO nanostructures.

2.3. Characterization of Mn Doped ZnO Nanostructures

The morphological investigation of Mn doped ZnO nanostructures was done by field emission scanning electron microscopy, FEI Quanta 200 FEG coupled with the energy dispersive spectroscopy (Hillsboro, OR, USA). The structural characterization was done by X-ray diffractometer (XRD, Bruker, Billerica, MA, USA) “Bruker D8 Discover” measured with Cu-K radiations ($\lambda = 1.54178 \text{ \AA}$) in the range of 10–80° with scan speed of 8°/min. The optical and photocatalytic properties of as-synthesized nanostructures were examined at room-temperature using UV-Visible spectroscopy (Carry-100, Bio UV-vis spectrophotometer) Agilent Technologies (Santa Clara, CA, USA), while the sensing studies of CIP were performed by using photoluminescence spectra (Perkin Elmer LS55, Perkin Elmer, Waltham, MA, USA).

2.4. Luminescent Sensor Evaluation

Mn-doped ZnO nanostructures were utilized to fabricate a luminescent sensor for the sensing of ciprofloxacin. Ciprofloxacin (1-cyclopropyl-6-fluoro-1,4-dihydro-4-oxo-7-(piperazinyl)-3-quinoline carboxylic acid), with a formula $C_{17}H_{18}FN_3O_3$ is an antibiotic used to treat a number of bacterial infections. The structure of ciprofloxacin is shown in Figure 1. The obtained Mn-doped ZnO nanostructures were dispersed in double-distilled water (1.5 mg metal oxide in 50 mL H_2O) and 5 mM stock solution of ciprofloxacin was prepared. All the solutions were prepared in double-distilled water and were kept for approximately half an hour before conducting the experiment. The prepared standard dilution of ciprofloxacin was quantified by fluorescence intensities. The calibration curve was constructed by plotting the analyte intensity against the concentration. Sensing application was performed at various concentrations of ciprofloxacin ranging from 2.0 to 44.0 μM .

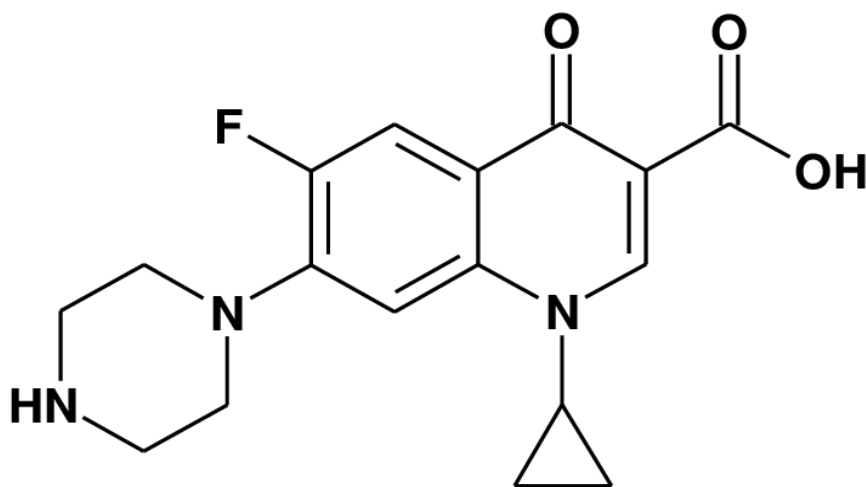


Figure 1. Chemical structure of ciprofloxacin.

2.5. Photocatalytic Properties of Mn-Doped ZnO Nanostructures toward Methyl Orange (MO)

The photocatalytic activity of Mn-doped ZnO nanostructures was studied by using a degradation reaction of methyl orange (MO), which is an azo dye. In a typical reaction procedure, the experimental solution is irradiated with UV rays (125 W Mercury lamp) by using different concentrations of synthesized nanostructures. The samples of the experimental solution were collected at regular intervals of time and analyzed with the help of UV-visible spectrophotometer. The rate of degradation for the decomposition of MO was estimated by evaluating the change in absorbance at $\lambda = 465$ nm in the UV-Vis spectra. The percentage degradation of MO dye was estimated as shown in Equation (1):

$$\text{Percentage degradation} = \frac{A_0 - A}{A_0} \times 100 \quad (1)$$

where A_0 is the initial absorbance of MO and A stands for the absorbance of dye at a certain reaction time ' t '.

3. Results and Discussion

3.1. Characterization of Mn-Doped ZnO Nanostructures

The surface morphology of the synthesized Mn-doped ZnO has been shown in Figure 2a,b. Figure 2a is the low magnification, while Figure 2b is the high magnification FESEM images of Mn-doped ZnO. A careful observation of Figure 2a reveals that synthesized nanoparticles were agglomerated and grown in very high density; however, Figure 2b reveals the formation of a highly porous structure with merged grain boundaries. The crystal structure of the synthesized Mn-doped

ZnO analyzed by using XRD is shown in Figure 2c. Figure 2c contains various well-defined diffraction peaks at $2\theta = 31.81^\circ, 34.41^\circ, 36.31^\circ, 47.61^\circ, 56.61^\circ, 63.11^\circ, 66.48^\circ, 68.11^\circ, 69.21^\circ, 72.41^\circ$, and 76.91° corresponding to the planes (100), (002), (101), (102), (110), (103), (200), (112), (201), (004), and (202), respectively, which are related with the wurtzite hexagonal phase. From the XRD spectra, it has also been observed that the diffraction peaks can be attributed to crystalline ZnO, and no peak of Mn appears in the spectra, which clearly indicates that the lattice structure remains intact [51]. The data were in good agreement with the Joint Committee on Powder Diffraction Standards (JCPDS) card for ZnO (JCPDS 036-1451) [52]. The elemental analysis of the synthesized Mn-doped ZnO nanostructures was investigated with the help of EDS and shown in Figure 2d. A close observation of Figure 2d clearly confirmed that the synthesized nanostructures contained zinc (Zn), oxygen (O), and manganese (Mn). Furthermore, no other peak related to any other element was found, which clearly indicate that the synthesized material is free from impurities up to the detection capability of EDS.

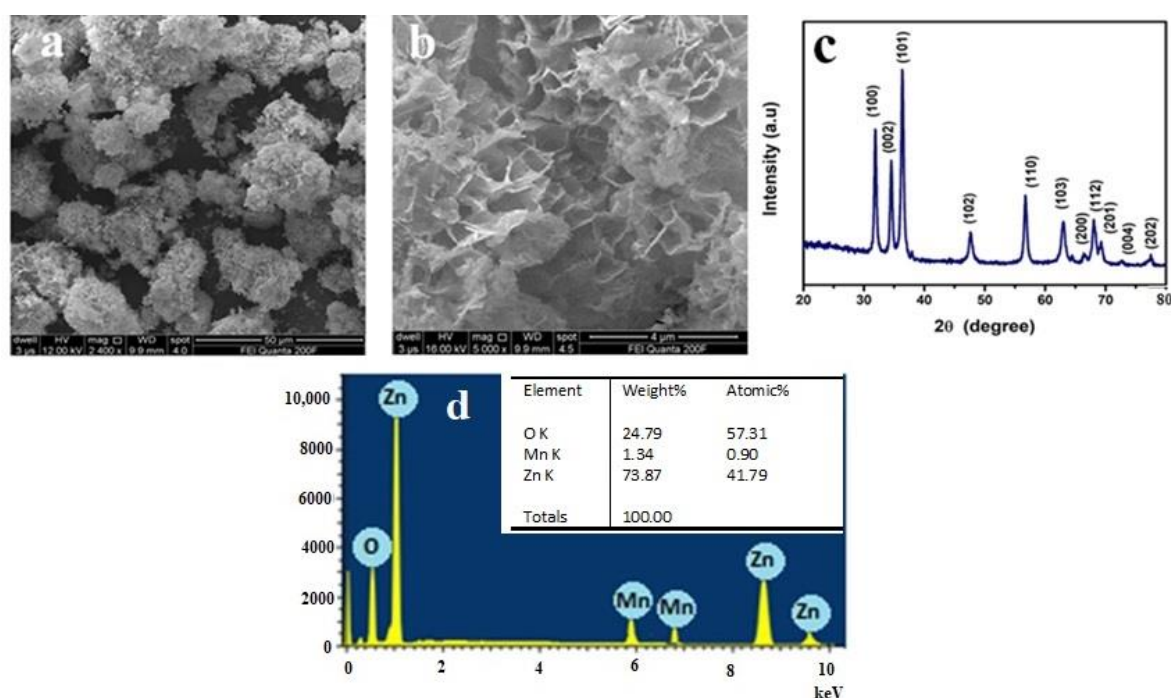


Figure 2. Typical (a) low-magnification and (b) high magnification FESEM images; (c) XRD and; (d) energy-dispersive X-ray spectroscopy (EDS) spectrum of synthesized Mn doped ZnO.

Analysis of the optical quality of the ZnO nanoparticles is very important due to its wide band gap 3.37 eV and a large exciton binding energy 60 meV, which makes it a unique electronic and photonic semiconducting material [47,48]. The optical activity of Mn-doped ZnO nanostructures was analyzed by using absorption spectra (UV-visible), as shown in Figure 3a. It was well known that the spectrum of undoped ZnO shows a single absorption peak at around 367 nm (figure not shown). A similar peak at 367 nm of undoped ZnO was already reported in the literature. Meanwhile, Mn-doped ZnO nanostructures show the red shifts (391 nm) compared to ZnO (367 nm). This shift of the absorption edge confirms the size elevation of Mn-doped ZnO. The band gap energy (E_{bg}) has been calculated by using Equation (2) [51],

$$E_{bg} = 1240/\lambda_{max} \quad (2)$$

where E_{bg} is the direct band gap energy and λ_{max} is the absorption wavelength (391 nm) of the Mn-doped ZnO nanostructures. The band gap energy of Mn-doped ZnO nanostructures has been calculated by using the maximum absorption wavelength. The band gap energy calculated by using the above equation has been found to be 3.17 eV. The red shift in the presence of Mn ions that has been

observed in the absorption maxima is attributed to the decrease in the band gap energy, which makes it a better candidate for photocatalytic activities.

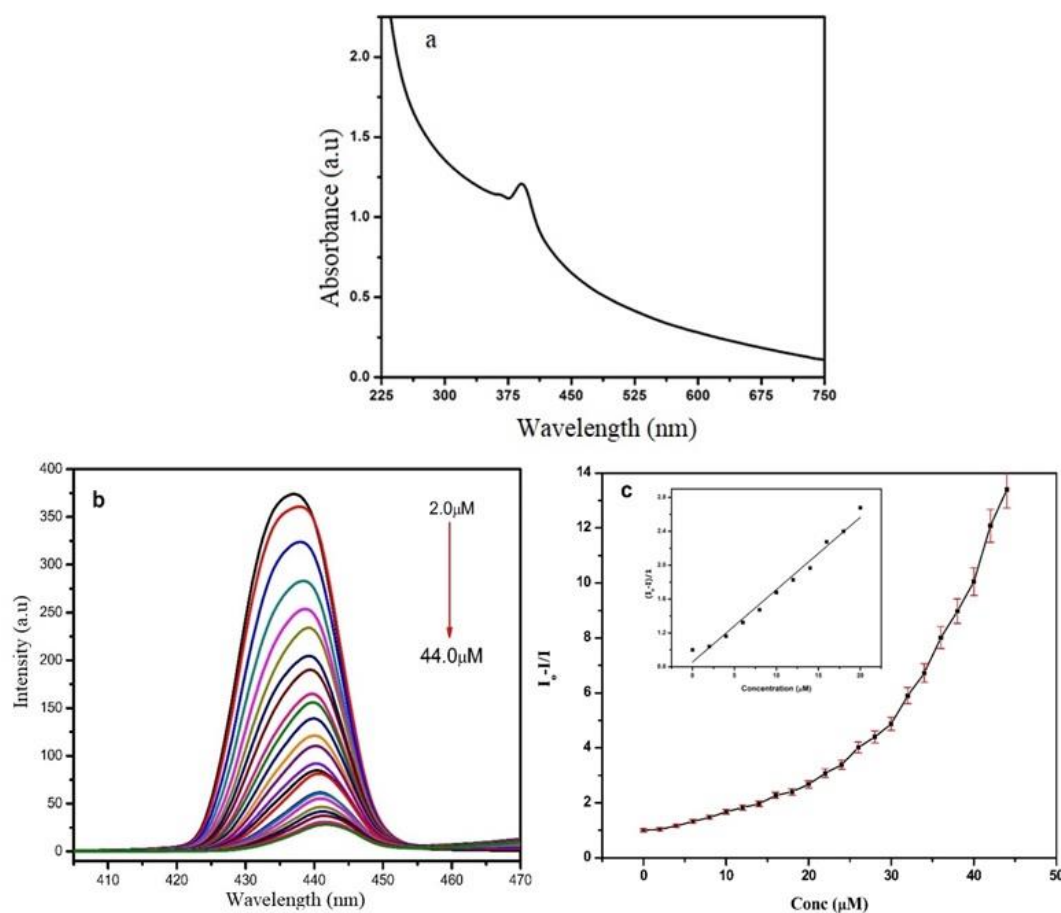


Figure 3. (a) Typical UV–visible spectrum of Mn-doped ZnO nanostructures. (b) Effect of ciprofloxacin concentration (2.0–44.0 μM) on the fluorescence emission spectra of prepared Mn-doped ZnO nanostructures; and (c) typical plot of $(I_0 - I)/I_0$ versus the concentration of ciprofloxacin; the inset shows that the relative intensity $(I_0 - I)/I_0$ follows a linear range up to 20 μM concentration of ciprofloxacin. Vertical error bars represent the standard deviation from the mean.

3.2. Mn-Doped ZnO Nanostructures as Fluorescent Sensor for Ciprofloxacin

In the first step, the synthesized Mn-doped ZnO nanostructures were analyzed for the stability by using fluorescence spectrophotometer. It has been found that there is no change in the intensity as well as the position of the peak, even after a time of 20 days. In other words, there is no change in the photoluminescence (PL) spectra. Then, these nanostructures have been utilized for the fluorescence sensing of ciprofloxacin. In the second step, the PL spectra of these nanostructures were recorded at different excitation wavelengths ranging from 330 to 410 nm with a regular gap of 10 nm in order to find out the excitation value at which the $\lambda_{\max}$ (380 nm) is shown by these nanostructures. In the third step, we perform the sensing experiment; in this case, the photoluminescence sensing studies were carried out by using 3 mL solution (1.5 mg in 50 mL) of synthesized Mn-doped ZnO nanostructures followed by the successive addition of the different amounts of the analyte ciprofloxacin. The response of PL quenching for Mn-doped ZnO nanostructures for each amount of the analyte (ciprofloxacin) is examined at least three times, and the average result has been illustrated in Figure 3b. Relative standard deviation has been estimated as $\approx 5\%$. From Figure 3b, it has been clearly visible that the PL intensity of Mn-doped ZnO nanostructures decreases with the increase in concentration of ciprofloxacin, which clearly indicates the binding of analyte to the surface of nanoparticles.

To get the exact information about the quenching process, we have used the Stern–Volmer Equation (3) [53],

$$\frac{I_0}{I} = K_{sv}[Q] + 1 \quad (3)$$

where I_0 and I correspond to the intensities before and after the addition of ciprofloxacin, respectively, K_{sv} is the Stern–Volmer quenching constant, and $[Q]$ is the concentration of quencher. Figure 3c shows the variation of (I_0-I/I) versus the concentration of the quencher, ciprofloxacin. From Figure 3c, it has been observed that Stern–Volmer plots show mixed behavior (linear as well as non-linear) over the entire concentration range of the quencher, ciprofloxacin. The linearity was evaluated by the least square regression method. The responses for ciprofloxacin were found to be linear in the concentration range of 2–20 μM with a correlation coefficient (R^2) value of 0.981. Linear behavior has been observed on increasing the concentration upto a certain level, which implies the dominance of the static quenching over the dynamic quenching process. Linearity has been observed when the intensity ratio (I_0-I/I) is plotted with a concentration of ciprofloxacin up to 20 μM with a regression coefficient of 0.981, whose value starts decreasing as the concentration increases beyond 20 μM (Inset Figure 3c). However, any further increase in concentration leads to the upward curvature, which simply means the coexistence of both types of quenching by the same quencher [53,54].

To resolve this ambiguity, on account of the non-linear response of intensity ratio with the concentration of analyte, a modified Stern–Volmer equation has been suggested, as shown in Equation (4) [55,56]

$$\frac{I_0}{I} = K_{sv}[Q]e^{V[Q]} + 1 \quad (4)$$

Equation (4) can further be simplified as follows in Equation (5):

$$\frac{I_0 - I}{Ie^{V[Q]}} = K_{sv}[Q] \quad (5)$$

where V represents the static quenching constant, and its value has been obtained from Equation (4) by plotting $\frac{I_0-I}{Ie^{V[Q]}}$ versus $[Q]$ by varying V until a linear response is obtained, as shown in Figure 4a. Figure 4a shows a linear fit of the plot $\frac{I_0-I}{Ie^{V[Q]}}$ versus ciprofloxacin concentration with a regression coefficient of 0.947 with a value of V fits to 0.0419 for the Mn-doped ZnO nanostructure. The detection limit is determined by the analysis of sample with known concentrations of analyte and by establishing the minimum level at which the analyte can be reliably detected. Determination of the LOD is based on the use of the calibration curve of the sensor and on the IUPAC recommendation, which states that the LOD can be obtained from the sensor calibration curve by considering the standard deviation (σ) of the blank measurement three times ($3\sigma_{\text{blank}}$). Similar methods were also reported by other researchers for the calculation of LOD [57,58]. The limit of detections calculated was found to be 10.05 μM for the Mn-doped ZnO nanostructure.

3.3. Selectivity of Mn-Doped ZnO Nanostructures

In order to study the selectivity of the as-prepared Mn-doped ZnO nanostructures, different organic compounds are tested in the presence of ciprofloxacin at the same concentration of 30 μM , and the results are depicted in Figure 4b. Figure 4b shows that the relative PL intensity for the ciprofloxacin ion is exceptionally high as compared to other analytes (phenol, aniline, benzylalcohol, benzonitrile, and benzaldehyde) at the same concentration of 30 μM at RT, which clearly reveals that except for ciprofloxacin, none of the other organic analytes (phenol, aniline, benzylalcohol, benzonitrile, and benzaldehyde) are able to quench the photoluminescence spectra of the as-prepared Mn-doped ZnO. Since ciprofloxacin has more ability to bind due to its structure, it forms a chelate-type interaction with the nanostructure Mn-doped ZnO. In other words, the influences of other analytes (phenol, aniline, benzylalcohol, benzonitrile, and benzaldehyde) are almost negligible as compared to ciprofloxacin in the sensing system. Thus, the observed results confirmed that the fabricated luminescence sensor

exhibits good selectivity toward ciprofloxacin. The detection method is sensitive with a limit of detection close to 10 μM level of ciprofloxacin in aqueous solution. In addition, the detection method is highly selective to ciprofloxacin over other potentially competing analytes in aqueous solution. Moreover, it can be concluded that this simple detection method can be used to measure the amount of ciprofloxacin in urine or other samples without any pretreatment or separation steps by using Mn-doped ZnO nanostructures. Thus, with some more detailed study, the present suggested detection method could be possibly be applied to measure the bioavailability of ciprofloxacin and hence to control drug overdose and to study drug pharmacokinetics by commercializing the large-scale production of a sensor.

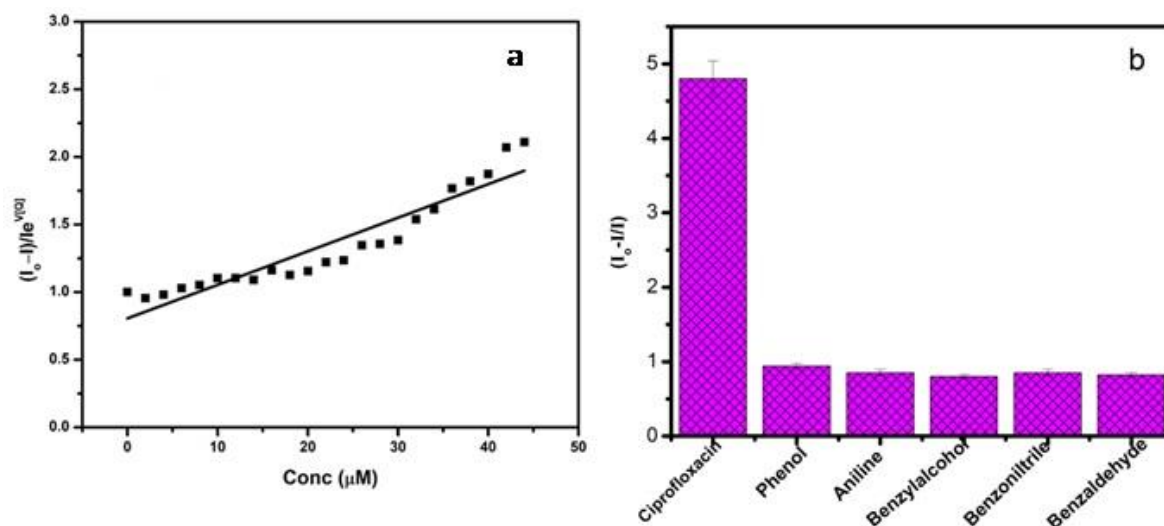


Figure 4. (a) Modified Stern–Volmer equation plot for different concentrations of ciprofloxacin; (b) $I_0 - I/I$ of Mn-doped ZnO solution when different aromatic molecules are present at constant concentration. Vertical error bars represent the standard deviation from the mean.

3.4. Photocatalytic Activity against Methyl Orange (MO)

The photocatalytic properties of the synthesized Mn-doped ZnO nanostructure have been analyzed against methyl orange, which is an azo dye, under UV light illumination. In the first step, before conducting the experiment in UV light, 100 mL of 10 ppm MO dye solution and Mn-doped ZnO nanostructures at RT were stirred for 30 min in dark so that the loss of dye due to the absorption/adsorption can be taken into account. Then, in the second step, the experimental solution was exposed to a 125 W mercury vapor lamp. In order to study the rate of degradation of dye, we have collected the sample of the experimental solution, which was analyzed in terms of absorbance data that were recorded at regular time intervals. The MO dye degradation was studied by using different concentrations (0.05, 0.10, and 0.15 g) of the Mn-doped ZnO nanostructure. By detailed experiments, interestingly, it was observed that with increasing the photocatalyst amount, i.e., Mn-doped ZnO, the dye degradation also increases. Figure 5a represents the variation of relative concentration (A/A_0) versus time interval over which the photodegradation of MO was studied by using different dosages of Mn-doped ZnO nanostructures under UV irradiation. It is apparent from the Figure 5a that no significant photodegradation was observed when the experimental solution contained Mn-doped ZnO nanostructures but there was no UV light irradiation. The decrease in the absorbance value was attributed to the adsorption–desorption equilibrium. While in the presence UV light, MO degraded significantly. Interestingly, it has been observed that the photodegradation rate of MO increases constantly with increasing the amounts of as-synthesized photocatalyst, which confirms that the as-synthesized Mn-doped ZnO nanostructures are effective catalysts for the photocatalytic degradation of MO. Figure 5b demonstrates the plot for percentage of photodegradation versus time interval for the photodegradation of MO over Mn-doped ZnO nanostructures under UV irradiation. In the presence

of 0.15 g of Mn-doped ZnO nanostructures under UV illumination, a significant degradation ($\approx 85\%$) of MO dye was observed in 75 min. It was observed after 75 min of UV illumination, the MO color changes from the original red/orange color to colorless, as shown in the inset of Figure 5b. This further confirms that the prepared Mn-doped ZnO nanostructures are effective and promising photocatalysts that can be used for the photocatalytic degradation of a range of hazardous dyes and chemicals. The crystalline size, specific surface area, morphologies, and textures are the most important factors that determine the photocatalytic performances of a catalyst [59]. Among these factors, the structural morphology generates a vital impact on the photocatalytic performance, as the photocatalytic activity depends on some specific exposed crystal faces [60]. As the exposed surfaces of each nanostructure vary with their morphologies, hence, Mn-doped ZnO becomes a more active photocatalyst, if it has more specific sites. In the current work, it is clear from the obtained morphologies, i.e., Mn-doped ZnO, a porous nanostructure exhibit higher surface-to-volume ratios and hence present excellent photocatalytic properties toward the photocatalytic degradation of MO.

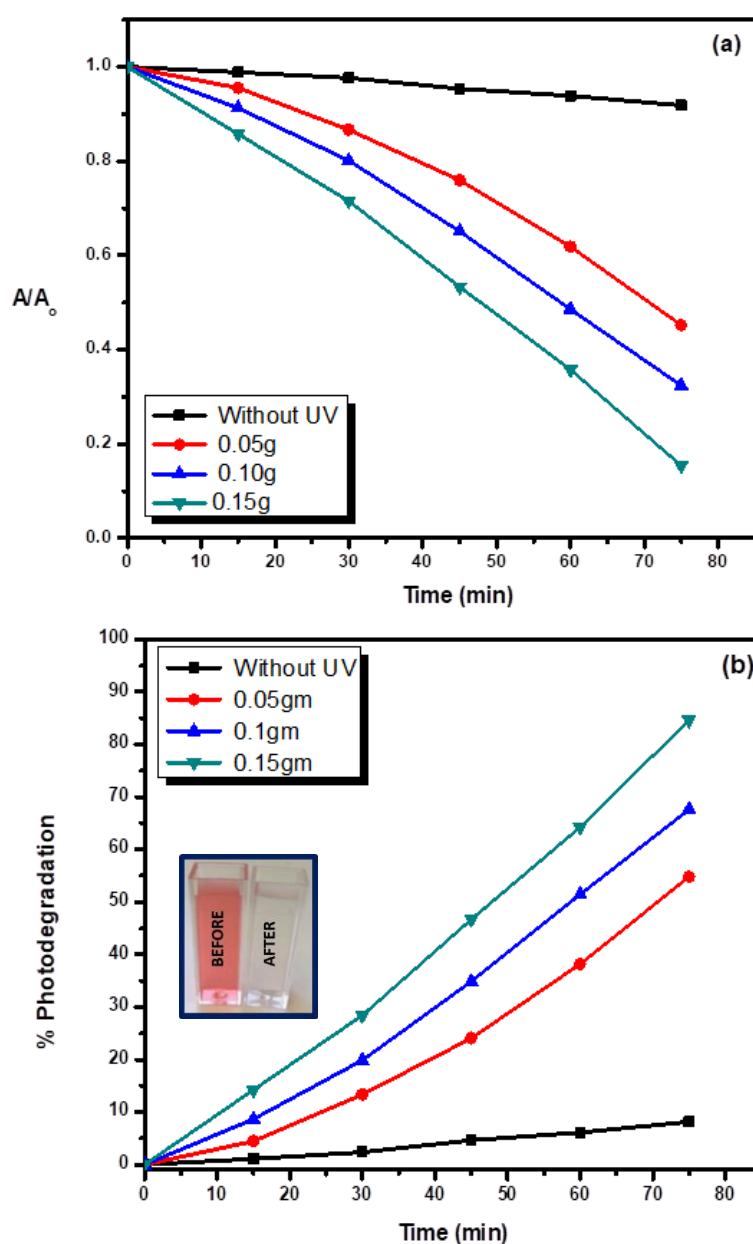


Figure 5. (a) Represents the extent of decomposition (A/A_0) and (b) the percentage photodegradation of MO under UV irradiation with respect to irradiation time.

3.5. Reusability Studies of Mn-Doped ZnO Nanostructure

The photocatalytic efficiency of the recycled nanostructures was carried out by collecting the Mn-doped ZnO nanostructure used in the first cycle. Then, these nanostructures were dispersed in 100 mL deionized water, followed by the centrifugation for 10 min at 10,000 rpm. To ensure the removal of trace amounts of dye adsorbed on the nanostructure surface, the whole process was repeated five times. Figure 6 shows that the efficiency of the recycled Mn-doped ZnO nanostructure (0.15g) was very similar to that of the initial one. However, overall, no significant reduction in the percentage photodegradation of MO was observed. The result of the reusability of the Mn-doped ZnO nanostructure indicates that the spent Mn-doped ZnO nanostructure can be reused without losing much of its percentage of photodegradation efficiency (Figure 6); this implies that the Mn-doped ZnO nanostructure is stable and possesses good reusability ability and will enhance cost reduction for application in the industry.

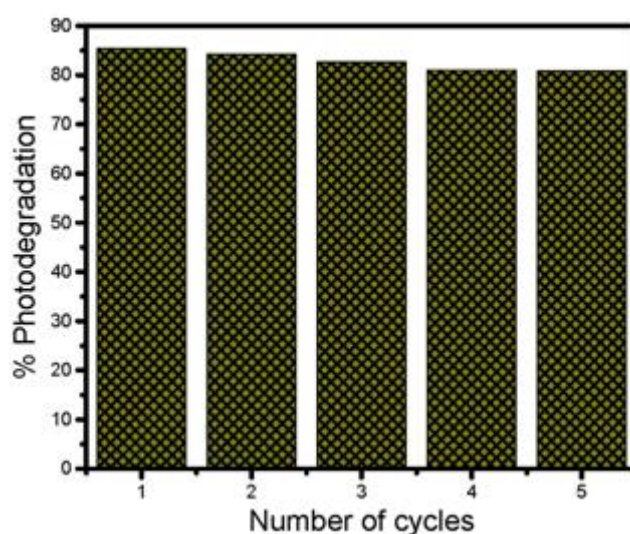


Figure 6. Represents the percentage photodegradation of methyl orange under UV irradiation w.r.t. irradiation time using recycled Mn-doped ZnO nanostructures.

3.6. Plausible Mechanism for the Photocatalytic Degradation of MO

The photocatalytic superiority of the Mn-doped ZnO nanostructures over the other nanostructures can be attributed to their structural features. Mn^{2+} doping in the ZnO generates new energy states called defect states, as shown in Figure 7, which acts as an intermediate for the transition of the valence band electron and results in an increase in the absorption of light as well as a decrease in the recombination rate [44]. Then, the conduction band electrons (e_{CB}^-) and valence-band holes (h_{VB}^+) generated due to the UV light of suitable frequency are reached on the surfaces of Mn-doped ZnO nanostructures for a further reaction. On the surface, holes as well as electrons can react with water molecules close to the surface of Mn-doped ZnO nanostructures, which leads to the formation of highly reactive hydroxyl radicals (as shown in the Scheme 1), which are a powerful oxidizing agent that oxidized the dye molecules into water and carbon dioxide as products. The decrease in size increases the porosity, which increases the surface area and results in an increase in the charge-transfer rates and a decrease in the recombination rate of the photogenerated electron/hole pairs. All of these processes ultimately lead to the enhanced photocatalytic efficiency in the degradation of organic pollutants. The photocatalytic reaction during the photocatalytic degradation of MO dye using Mn-doped ZnO nanostructures can be written as shown in Scheme 1.

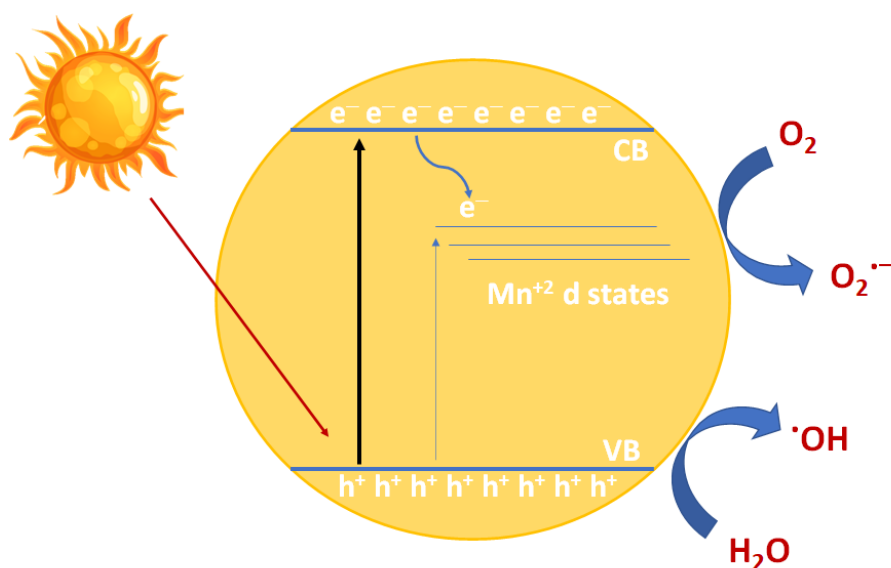
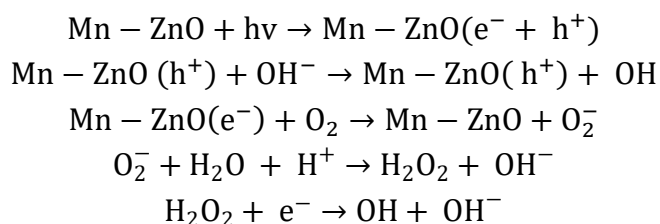


Figure 7. Photocatalytic degradation mechanism for the photocatalytic degradation of MO in the presence of Mn-doped ZnO nanostructures.



Scheme 1. Mechanism for the degradation of organic dye molecule.

4. Conclusions

In summary, we have successfully synthesized Mn-doped ZnO nanostructures via a facile solution combustion process. The synthesized Mn-doped ZnO nanostructures were characterized by using various characterization techniques, which reveal the large-scale synthesis of well-crystalline nanoparticles and the successful incorporation of Mn ions in the ZnO matrix, which show excellent chemical sensing as well as photocatalytic properties. Mn-doped ZnO nanostructures were found to show a low LOD value, i.e., 10.05 μM for ciprofloxacin sensing. Furthermore, when analyzed for interfering studies, the developed sensor exhibits good selectivity toward ciprofloxacin in the presence of other interfering organic molecules. Moreover, when the synthesized material was analyzed as a photocatalyst against MO, it has proven its superior activity as a photocatalyst. The 85% degradation of MO has been achieved just in 75 min using 0.15 g of Mn-doped ZnO nanostructures. Thus, the presented work clearly demonstrates that Mn-doped ZnO nanostructures synthesized by solution combustion methods are an excellent sensing material against ciprofloxacin as well as an efficient photocatalyst against MO dye.

Author Contributions: Methodology, writing—original draft preparation, D.T.; visualization, Supervision, A.S.; writing—review and editing, A.A., D.S.R., D.S., S.P. and S.T.; Visualization, formal analysis, interpretation, resources, funding acquisition, S.P. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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