Mn-doping-induced photocatalytic activity enhancement of ZnO nanorods prepared on glass substrates


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ABSTRACT

Mn-doped ZnO nanorods were synthesized on glass substrates via a two-steps process of ultrasonic spray pyrolysis and hydrothermal methods with four different concentrations Mn-doping (0, 1, 3, and 7 mol%). Introduction of Mn into ZnO is known could enhance the photocatalytic activity owing to the increase in the defect sites that effectively suppress the recombination of free electrons and holes. In this study, results show that Mn-doping has effectively modified the nucleations and crystal growth of ZnO, as evidenced by the increasing in the diameter, height, and the number of nanorods per unit area, besides slightly reduced the band gap and increased the oxygen vacancy concentrations in the ZnO lattice. This condition has successfully multiplied the photocatalytic performance of the ZnO nanorods in the degradation of methylene blue (MB) compared to the undoped-ZnO sample where in the typical process the MB can be degraded approximately 77% within only 35 min under a UV light irradiation.

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1. Introduction

ZnO is a wide-bandgap semiconductor (3.37 eV) that has a large exciton binding energy at room temperature (60 meV) [1]. ZnO has attracted considerable attention because it is low cost, non-toxic, environmentally friendly, chemically stable, and its optical and electrical properties can be tuned via doping [2,3]. ZnO has several potential applications, such as photocatalysts, light emitting diodes, solar cells, and sensors [1,4-6]. Photocatalytic reaction is a reduction-oxidation process that occurs on the surface of the photocatalyst, which can be used for degrading harmful organic pollutants, such as textile dyes. Several methods have been proposed to enhance the photocatalytic activity of ZnO. One of these methods involves doping ZnO with non-metal and metal elements [7-17]. Doping of transition metal ions, such as Mn, Fe, Co, Ni, and Cu, into ZnO has been reported to reduce the bandgap energy and to prevent electron-hole pair recombination through the generation of new energy states [18-25]. The transition metal Mn is an interesting material because the radius of Mn$^{2+}$ is similar to that of Zn$^{2+}$, and it can therefore easily replace Zn$^{2+}$ ions without resulting in any significant crystal changes [7]. Many research groups have reported that the introduction Mn into ZnO could enhance the photocatalytic activity under UV and visible irradiation and this is attributed to the increase in the number of defect sites acting as electron traps that effectively suppresses the recombination of the photogenerated carriers [18,21,26-30]. Very few reports have observed the effect of Mn dopant on its morphological properties and photocatalytic activity. Recently, Qun Ma et al. reported that the incorporation of Mn dopants can greatly affect the transformation of the hierarchical ZnO structure and its photocatalytic performance [26]. Moreover, Mn-doped ZnO was generally synthesized in the form of powder with macro-scale size [26,28,29,31] or nanoparticles [18,21,30,32]. The use of ZnO powder as a photocatalyst is less effective, because it requires some additional process such as centrifugation to separate the ZnO powder from the polluted water. Therefore, some researchers have developed ZnO nanorods grown on substrates to improve the photocatalyst efficiency [33-35].

In this experiment, Mn-doped ZnO nanorods were synthesized onto glass substrates by using low-cost and simple methods. ZnO nanorods were strongly bound to the substrates since the growth process was preceded by a seeding process via the ultrasonic spray pyrolysis method. Then, ZnO nanorods were grown on ZnO thin layers by hydrothermal methods. The ZnO photocatalytic activity was evaluated through photodegradation process of methylene
blue (MB) under UV radiation. For nanorods on the surface of substrate, it will be easier to observe the morphological changes of ZnO due to the presence of Mn dopant. Therefore, the analysis of the enhancement of photocatalytic activity of Mn-doped ZnO not only based on its microstructural and optical properties as widely reported previously, but also its morphological properties. This result directs to an interesting advantage to control the growth rate and morphological properties of the ZnO nanostructures by varying the dopant concentration for various applications.

2. Experiments

2.1. Materials

Analytical grade zinc acetate dehydrate (C\textsubscript{5}H\textsubscript{4}O\textsubscript{2}Zn\textsubscript{2}H\textsubscript{2}O), zinc nitrate tetrahydrate (C\textsubscript{4}H\textsubscript{4}O\textsubscript{2}Zn\textsubscript{2}H\textsubscript{2}O), mangan (II) nitrate tetrahydrate (Mn(NO\textsubscript{3})\textsubscript{4}2H\textsubscript{2}O), and hexamethylenetetramine (C\textsubscript{6}H\textsubscript{12}N\textsubscript{4}), purchased from Merck, were used without further purification.

2.2. Synthesis

ZnO nanorods were synthesized directly on the glass substrates (15 mm × 25 mm) using two steps: seeding process via ultrasonic spray pyrolysis and growth process via hydrothermal methods, according to a previously reported procedure [11,36,37]. The seeding process began with dissolving 0.2 M zinc acetate dehydrate into deionized water in room temperature. The seed solution was then placed into a container in a commercial ultrasonic nebulizer (1.7 MHz) and then sprayed onto the heated glass substrates at 450 °C for 15 min. The samples were then annealed for 1 h at 450 °C. For the growth solution, equimolar 0.05 M zinc nitrate tetrahydrate and hexamethylenetetramine were dissolved in deionized water by stirring for 50 min at room temperature. The solutions were varied with four different Mn doping concentrations (0, 1, 3, and 7 mol\%) by using 0.05 M mangan nitrate tetrahydrate solution. Substrates containing the seed layers were then soaked in 10 ml growth solution and heated in an oven for 6 h at 95 °C.

2.3. Characterization

The surface and cross-section morphologies of the samples were determined by field emission scanning electron microscopy (FESEM; JEOL JIB-4610F Multi Beam System) together with energy dispersive X-ray analysis (EDAX; Oxford Instruments, UK). The surface area of ZnO nanorods were calculated manually from SEM images by multiplying the surface area of a nanorod by the number of nanorods appearing in a surface of substrate. The crystal structure was characterized by X-ray diffraction (XRD; Rigaku Smartlab 3 Kv), X-ray photoelectron spectroscopy (XPS) measurements were carried out using the ULVAC-PHI Quantera II with Al Kα X-ray beam at 14866.6 eV. Raman spectra measurements were carried out using the WITec Raman microscope equipped with a 532-nm laser source. The optical absorption and reflectance spectra were recorded using the Thermo Fisher Scientific GENESYS 10S Ultraviolet–Visible and UV–Vis Diffuse Reflectance U-3900H Spectrophotometer, respectively. The room temperature photoluminescence (PL) spectra were recorded with 325-nm He-Cd laser excitation using Edinburgh FLS 920. Electrochemical impedance spectroscopy (EIS) measurement was performed using an electrochemical impedance analyzer (EDAX; E100) embedded to a potentiostat (EDAQ; 163). Platinum wire was used as the counter electrode. Ag/AgCl was used as a reference electrode and the ZnO nanorods onto ITO coated glass substrate was used as the working electrode. All electrodes were soaked in a cell containing an electrolyte solution of 0.5 M sodium chloride (NaCl). The measurement was performed under UV light (40 W) using a sinusoidal ac perturbation of 250 mV over the frequency range of 1 Hz–100 kHz.

2.4. Photocatalytic activity measurement

The photocatalytic activity of the Mn-doped ZnO nanorods was evaluated by the photodegradation of MB dye in an acidic aqueous condition (pH 5). The ZnO samples were placed in 20 ml of 10 mM MB solution and irradiated with UV light (40 W). At certain time intervals, the samples were simply removed from the solution, and the optical absorption spectra were monitored using a UV–Vis spectrophotometer at the characteristic absorption peak wavelength of the MB dye at 596 nm. The reusability performance of ZnO photocatalyst was also evaluated via the same above procedure in five successive cycles.

3. Results and discussion

3.1. Morphological and structural analysis

Fig. 1 shows FESEM images of the surface morphology of the ZnO nanorods. All samples show that ZnO generally grows perpendicularly to the surface of the glass substrate in the form of hexagonal nanorods. In each sample, the diameter of the nanorods varies and tends to increase with an increase in the Mn concentration. The diameters of the ZnO nanorods without Mn are in the range of 100–180 nm, whereas the diameters of the ZnO nanorod with 1 mol% Mn are in the range of 110–250 nm. The samples of 3 and 7 mol% Mn-doped ZnO are not significantly different compared to the samples of 1 mol% Mn-doped ZnO, but they are characterized with dominant nanorods with diameter larger than 200 nm. Apart from the increasing diameter, the addition of Mn dopant also increases the number of nanorods per unit area. The number of pure ZnO nanorods is around 13 μm\textsuperscript{2}, while the number of ZnO nanorods with 1, 3, and 7 mol% Mn is around 17, 20, and 21 μm\textsuperscript{2}, respectively. The calculated surface area of ZnO nanorods with 0, 1, 3, and 7 mol% Mn is around 10, 16, 20 and 26 μm\textsuperscript{2} per μm\textsuperscript{2} substrate, respectively.

Moreover, cross-sectional images of the nanorods are shown in Fig. 2. It can be seen that the average height of the ZnO nanorods increases with an increase in the Mn concentration. The mean height of the ZnO nanorods with 0, 1, 3, and 7 mol% Mn is 1.74, 1.82, 2.01, and 2.27 μm, respectively. It is also seen that the diameter of the nanorods increases with the addition of Mn, which is in accordance with the surface image shown in Fig. 1. The effect of Mn dopant on the morphology of ZnO has also been reported previously [7,38]. Panigrahy et al. reported that doping of 5 mol% Mn increased the diameter of ZnO nanorods from 85 to 150 nm [39] and 2 at.% Mn increased the diameter range of ZnO nanorods from 120–400 nm to 120–700 nm [40]. These SEM images clearly show that Mn elements may induce an enhancement of the ZnO crystal growth, as evidenced by the increase in the diameter, height, and the number of nanorods per unit area that resulted in the increase in the ZnO surface area.

As already known that the shape and orientation of ZnO nanostructures fabricated by solution method is strongly correlated with the degree of supersaturation [41]. It is also believed that in low supersaturation levels favors crystal growth while in high supersaturation level favors nucleation [42]. For ZnO hexagonal wurtzite structure in low supersaturation condition, the nanorods with (001) plane is the preferential growth due to it has the minimum surface free energy [43]. Many experimental works found that the dopants play an important role for controlling degree of supersaturation [41,44–46]. Based on Sethuraman's experimental work, the addition of Mn up to 7% could increases the degree of
The increase of Mn dopant decreases the crystal growth rate. During the growth process, the decrease of the dopant stimulates the new nucleation and accelerates the formation of the nanobath structure. The high aspect ratio of Mn nanowires with a preferential (001) orientation accelerates the new nucleation. The growth of Mn nanowires is hindered by the existence of the existing Mn nanowires, and the growth of Mn nanowires is hindered by the existing Mn nanowires. This condition may be favorable for Mn nanowires growth and nucleation.
Fig. 3a–c shows the EDAX spectra of Mn-doped ZnO nanorods. The elements of Zn, O, Si and Mn are present in all samples, where Si comes from the glass substrate. The chemical compositions are measured and it is indicated that the dominant elements are Zn (86.3–86.5 wt%) and O (13.1–13.5 wt%). Manganese (Mn) is detected in each sample with very small concentration (0.0–0.1% wt%) hence it cannot show the Mn concentration in ZnO when the amount of Mn was changed during synthesize. But from the elemental map on the right of each figure, it appears that Mn element is uniformly distributed throughout the surface of ZnO nanorods.

XRD patterns of the ZnO standard and Mn-doped ZnO nanorods are shown in Fig. 4. Based on the reference ICDD 98-005-7478, the XRD patterns show that all samples are composed of ZnO with wurtzite hexagonal structure. All the diffraction peaks at angles 2θ = 31.7, 34.4, 36.2, 47.5, 62.8, and 67.8 correspond to the reflection from the (100), (002), (101), (102), (103), and (112) crystal planes. There are no peaks associated with the Mn-related secondary phases or impurities. The peak intensities of those nanorods are almost similar for all variants of Mn concentrations, which indicates that an increase in the doping concentration does not alter the preferred crystal orientation of the nanorods arrays.

Fig. 4 shows that the highest diffraction peak of all samples is the (002) crystal plane, which indicates that the preferred orientation of the ZnO nanorods is perpendicular to the substrate. This confirms the morphological images as shown in Fig. 1. Therefore, the preferred orientation is measured qualitatively by the texture coefficient (TC) parameter using the following equation [47]:

\[ \text{TC}_{(hkl)} = \frac{I_{(hkl)}}{I_{(002)}} \left( \sum_{n=1} \frac{I_{(hkl)}}{I_{(002)}} \right) \]
where \(I(h k l)\) and \(I_0(h k l)\) represent the measured relative intensity and the standard intensity of plane \((h k l)\), and \(N\) represents the number of peaks. Table 1 shows the TC values of ZnO nanorods with 0, 1, 3, and 7 mol% Mn along six different diffraction planes. All samples have the highest TC value for the \((0 0 2)\) plane, suggesting that all the samples have c-axis preferred orientation, as shown in Fig. 1.

The preferred orientation \((0 0 2)\) plane in the XRD patterns was then used as a data source for calculating the lattice parameters, d-spacing, crystallite size, and FWHM, as shown in Table 2. In general, the lattice parameter, volume, and d-spacing are similar, and this is probably because the Mn\(^{2+}\) radius is similar to the Zn\(^{2+}\) radius so it easily substitutes Zn\(^{2+}\) without any significant crystal changes [7,39,48]. The crystalline size was calculated from the full-width at half-maximum (FWHM) by using the Debye-Scherrer formula [49]:

\[
D = \frac{0.91}{B \cos \theta}
\]

where \(D\) is the crystallite size, \(\lambda\) is the X-ray wavelength in Ångstrom, \(\theta\) is the Bragg angle, and \(B\) is the FWHM. The addition of Mn increases the crystalline size significantly from 18.7 to 46.5 nm. This increase, as in the case of the other previous results, is generally due to the ionic radius of Zn\(^{2+}\) (0.74 Å) being smaller than that of Mn\(^{2+}\) (0.80 Å) [26,48,50-52], while some reports state that Mn doping decreases the crystallite size of ZnO [28,53]. Furthermore, the position of \((0 0 2)\) peaks shift toward the lower and higher angle that strongly indicated that the Mn\(^{2+}\) ions successfully substitute the Zn\(^{2+}\) ions in the ZnO host structure [53-57].

XPS measurements were performed to identify the chemical states of the constituent elements and oxygen vacancies in the ZnO nanorods. Fig. 5 shows the XPS spectra of the undoped and Mn-doped ZnO \((7 \text{ mol} \% \text{ Mn})\) nanorods with an emphasis on the peaks associated with Zn 2p, Mn 2p, and O 1s. As shown in Fig. 5a and b, the spectra for Zn 2p3/2 and Zn 2p1/2 of the ZnO and Mn-doped ZnO samples exhibit symmetric single peaks. The binding energy of Zn 2p3/2 and Zn 2p1/2 of the pure ZnO is located at 1021.1 eV and 1044.2 eV, respectively, which correspond to Zn–O bonds in the ZnO lattice [18]. These two strong peaks indicate that Zn\(^{2+}\) is dominant in the ZnO structure [39,54]. The intensity of both peaks increased with the addition of Mn; this indicates that more Zn\(^{2+}\) ions are detected in the ZnO surface. This may be related to an increase in the surface area of ZnO nanorods, as shown in Figs. 1 and 2, which results in more Zn–O bonds being recorded by the XPS instrument. The binding energy of Zn\(^{2+}\) in Mn-doped ZnO also slightly shifts to 1021.5 eV and 1044.7 eV, which indicates that there is a partial substitution of Zn\(^{2+}\) by Mn\(^{2+}\) and that the Zn–Mn bonding structure is formed [51].

Fig. 5c shows that XPS spectra of O 1s could be decomposed into three peaks, namely lattice oxygen of ZnO with a binding energy of 529.95 eV, and the CO(O)=O bond at 531.13 eV, indicating the presence of oxygen vacancies, and at energy 532.52 eV, representing the existence of hydroxyl (COOH) bonds [31,51,58,59]. These hydroxyl bonds tend to stick to the empty space in the ZnO lattice [60,61]. Some authors reported that these hydroxyl bonds are related to the ZnO surface ability to absorb OH—groups and oxygen vacancies, which is useful for photocatalytic activity [51]. Meanwhile, Fig. 5d shows that the O 1s spectra of Mn-doped ZnO contain a new peak of MnO with the binding energy of 529.74 eV and that there is a shift peak of ZnO from 529.95 eV to 530.26 eV. This indicates that Mn element has been bound with the ZnO structure.

Fig. 5e shows that the XPS spectra of the Mn binding energy in the Mn-doped ZnO sample. There are two peaks of Mn 2p\(_{3/2}\) and Mn 2p\(_{1/2}\) with the binding energies of 640.7 eV and 655.8 eV, respectively. This indicates that Mn\(^{2+}\) ions are present predominantly in ZnO [62]. In addition, the Mn 2p\(_{3/2}\) peak intensity is higher than the Mn 2p\(_{1/2}\) peak intensity, which is different from previous result that the Mn 2p\(_{3/2}\) peak has a higher intensity than that of the others [58]. The reason for this is not clearly understood.

### Table 1

<table>
<thead>
<tr>
<th>Doping Concentrations</th>
<th>Crystal Plane</th>
<th>100</th>
<th>002</th>
<th>101</th>
<th>102</th>
<th>103</th>
<th>112</th>
</tr>
</thead>
<tbody>
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<td>Mn 0%</td>
<td></td>
<td>0.22</td>
<td>2.47</td>
<td>0.37</td>
<td>1.38</td>
<td>1.07</td>
<td>0.48</td>
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<tr>
<td>Mn 1%</td>
<td></td>
<td>0.28</td>
<td>2.53</td>
<td>0.54</td>
<td>1.05</td>
<td>0.83</td>
<td>0.78</td>
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<tr>
<td>Mn 3%</td>
<td></td>
<td>0.43</td>
<td>2.60</td>
<td>0.60</td>
<td>0.96</td>
<td>0.79</td>
<td>0.63</td>
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<tr>
<td>Mn 7%</td>
<td></td>
<td>0.24</td>
<td>1.99</td>
<td>0.46</td>
<td>1.56</td>
<td>1.08</td>
<td>0.68</td>
</tr>
</tbody>
</table>

### Table 2

<table>
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<th>Doping Concentrations</th>
<th>2θ</th>
<th>Volume ((Å^3))</th>
<th>(a = b \ (Å))</th>
<th>(c \ (Å))</th>
<th>(d_{002})</th>
<th>Crystallite size ((nm))</th>
<th>FWHM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn 0%</td>
<td>34.407</td>
<td>47.680</td>
<td>2.325</td>
<td>5.205</td>
<td>2.604</td>
<td>18.7</td>
<td>0.371</td>
</tr>
<tr>
<td>Mn 1%</td>
<td>34.410</td>
<td>47.690</td>
<td>2.325</td>
<td>5.205</td>
<td>2.604</td>
<td>43.1</td>
<td>0.296</td>
</tr>
<tr>
<td>Mn 3%</td>
<td>34.412</td>
<td>47.631</td>
<td>2.325</td>
<td>5.203</td>
<td>2.604</td>
<td>41.0</td>
<td>0.296</td>
</tr>
<tr>
<td>Mn 7%</td>
<td>34.386</td>
<td>47.679</td>
<td>2.323</td>
<td>5.203</td>
<td>2.606</td>
<td>46.5</td>
<td>0.293</td>
</tr>
</tbody>
</table>
yet, and hence, further analysis is required to identify the existence of other Mn ions with different electron valence conditions.

Fig. 6 shows the room temperature Raman spectra of the undoped and 7 mol% Mn-doped ZnO nanorods. The spectra reveal five modes of ZnO at 97, 330, 378, 437, and 575 cm⁻¹, corresponding to $E₂$(low), $E₂$(high) − $E₂$(low), $A₁$(TO), $E₂$(high), and $A₁$(low), respectively [39, 57, 58]. The $E₂$(low) mode involving a Zn sub-lattice motion [63], $E₂$(high) − $E₂$(low) is a second order mode of multi-phonon processes [63]. The high intensity of the $E₂$(high) mode indicates that all samples have good wurtzite hexagonal structure of ZnO [58, 64]. The higher intensity of $E₂$(high) in Mn-doped ZnO reveals that the Mn atom does not deform the crystal lattice of ZnO and even increases the crystallite sizes of ZnO, as shown in the XRD spectra. The $A₁$(low) peak relates to crystal defects, especially the oxygen vacancies [57, 58, 65]. The intensity of the $A₁$(low) mode also increases with the addition of Mn into ZnO, indicating that Mn doping increases the number of oxygen vacancies, which will be confirmed in the following photoluminescence measurement results.

![Fig. 5. XPS spectra of Mn-doped ZnO nanorods.](image_url)
Fig. 7: UV-Vis absorption spectra of Mn-doped ZnO nanocrystals.

The absorption edge is determined by the edge of the nanocrystals.

In order to obtain the correct UV-Vis diffuse-reflectance in the UV-Vis diffuse-reflectance spectra, the nanocrystals were recorded at room temperature as shown in Fig. 6.

The increase in the absorbance of UV-Vis diffuse-reflectance is caused by the increase in the absorption of ZnO nanocrystals. The increase in the absorbance of ZnO nanocrystals is caused by the increase in the absorbance of ZnO nanocrystals in the visible region between 400-550 nm.

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The room temperature PL spectra of undoped and Mn-doped ZnO nanorods are shown in Fig. 4.10. There are five prominent emission peaks at 397, 413, 450–475, 545–560, and 619 nm, while emissions in the range of 430–450 nm are believed to come from the glass substrate [72]. The addition of Mn elements generally increases the emission intensity of all peaks, especially in the visible region. The UV emission (397 nm) originates from the near band edge emission, which is due to the exciton recombination of the valence and the conduction bands of ZnO [73]. The emissions in the visible region are related to the native defects of ZnO, such as such as oxygen and zinc vacancies, interstitial Zn, interstitial O, Zn anti-site (zinc at oxygen site), and O anti-site (oxygen at zinc site) [66]. The violet emission (413 nm) is related to the Zn vacancy [74]. The blue...
emission (450–475 nm) is caused by the ZnO interstitial [7]. The green emissions (545–560 nm) is related to the oxygen vacancy, while the orange emissions (619 nm) is from the oxygen interstitial [76, 77]. ZnO nanorods with 7% Mn have the highest F. intensity in the visible region, indicating that they have more crystal defects and oxygen vacancies. In contrast, oxygen vacancies, or oxygen interstitials, are not observed in the green region, as shown in Figs. 7 and 10.

The electrochemical impedance measurement was performed to complete the information about the interface charge separation and charge transfer efficiency of ZnO nanorods. The interface layer of Mn-doped ZnO nanorods is shown in Fig. 11. The lower efficiency of charge transfer in Mn-doped ZnO nanorods with higher arc radius [78].
content of Mn reveals the arc with smaller diameter. This result shows that the interface layer resistances decrease as the more addition Mn on ZnO nanorods, indicating the higher efficiency of interfacial charge carrier's separation and charge transfer on the surface of ZnO. This agrees with optical characterization results that higher concentration Mn in ZnO nanorods could produce higher free charge carriers that accelerates charge transfer and decreases the resistance. It is beneficial for enhancement of photocatalytic activity of ZnO nanorods.

3.4. Photocatalytic activity

Photocatalytic activity of a catalyst is determined by its ability to create photogenerated electron-hole pairs [79]. Fig. 12 shows the absorption spectra of the MB solution with and without ZnO photocatalysts under UV irradiation for different durations of time until 38 min. It can be seen that MB is degraded for all kind of ZnO samples. The mechanism underlying the photocatalytic degradation of MB solution can be understood as follows. When ZnO samples are irradiated by UV, the electrons excite from the valence band to the conduction band forming free electrons and holes. These electron–hole pairs will react with the oxygen and water to produce (O$_2$) and (OH$^-$) free radicals. These highly reactive species are strong oxidizing agent that can react with MB dye and break its chemical bond structure resulting colorless form [83,80]. The MB degradation process by ZnO photocatalyst can be seen in the following reaction [73,63]:

\[
\text{ZnO} + \text{hv} \rightarrow e^-(\text{CB}) + h^+(\text{VB})
\]

\[
e^- + \text{O}_2 \rightarrow \text{O}_2^-
\]

\[
h^+ + \text{OH}^- \rightarrow .\text{OH}
\]

\[
.h^+ + \text{H}_2\text{O} \rightarrow .h^+ + .\text{OH}
\]

\[
.\text{OH} + \text{MB} \rightarrow \text{degradation product}
\]

\[
.\text{O}_2^- + \text{MB} \rightarrow \text{degradation product}
\]

The photocatalytic efficiency for the MB degradation was determined by using the following equation [63]:

\[
\eta = \frac{A_0 - A_t}{A_0} \times 100\%
\]

where $A_0$ is the original MB absorbance intensity value at 596 nm, and $A_t$ is the MB absorbance intensity value after the photodegradation at certain times. The results in Fig. 13 indicate that the degradation rates for the ZnO nanorods photocatalyst with 0, 1, 3, and 7 mol% Mn are 15.25%, 67.13%, 70.43%, and 76.75%, respectively. It is also seen that MB without the photocatalyst is slightly degraded with UV irradiation as a reference. It is clearly shown that the photodegradation rate of MB with the Mn-doped ZnO is faster than that with pure ZnO.

This improvement can be attributed to three factors. First, Mn elements may induce an enhancement of ZnO surface area, as evidenced by the increase in the diameter, height, and the number of nanorods per unit area, as shown in the SEM images. Meanwhile, the ZnO wurtzite structure is well-preserved, even the crystallites size are increased, as indicated by the XRD spectra and the enhanced intensity of XPS Zn2p and O1s and Raman spectra at 437 cm$^{-1}$. This morphological effect considerably increases the surface area of the ZnO and hence the generation of free electrons and holes for photodegradation of MB dye molecules are enhanced [73,81]. Second, Mn elements may lead the narrowing of band gap that is favorable for photoexcitation of more electrons from valence band to conduction band. Third, the Mn elements may also induce the increase of number of oxygen vacancies, as indicated by the decrease in the lattice constants, the increase in the $A_0$(low) peak in the Raman spectra, and the visible light emission. These crystal defects are also well known to inhibit the recombination process of electrons and free holes because Mn$^{2+}$ ions can act as electron traps or intermediate steps [7,18,48,52,81]. Donkova et al. reported that these doping ions would shift the Fermi level up to the bottom edge of the conduction band, which would increase the adsorption ability to the oxygen [26]. This synergistic effect actually depends on the Mn content in the ZnO because some reports indicate the opposite effect if the Mn content is not optimum [26,28,32,52].

The intensity of PL in all wavelength range may proportional to the photocatalytic activity. The higher PL intensity, the higher photocatalytic activity. It can be explained that in photoluminescence process, photogenerated electrons could recombine with holes and defects so those PL signals occur. Meanwhile, during the photocatalytic reaction, holes and defects could become the trap centers of photogenerated electrons hence the recombination could be effectively inhibited [82]. This is not contrary to the usual belief that a higher PL intensity indicates a higher recombination rate, since the luminescence intensity is also influenced by non-radiative recombination which do not affect the total recombination of charged carriers [24]. The above results demonstrate that the introduction Mn into the ZnO up to 7 mol% linearly escalate the surface area of

![Fig. 14. Photocatalytic activity of recycled Mn-doped ZnO nanorods.](image-url)
Application of Dosimeter

4 Conditions

Implementation of wireless monitoring and data transmission

To increase the adoption of ambient monitoring and supporting devices

References