Manganese doping on the structural properties of TiO₂ and ZnO nanoparticles

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Abstract. In this study, manganese (Mn) doped ZnO and TiO₂ were synthesized through the co-precipitation method. The Mn doping content was set at 6 atomic percent (at.%), and the physical properties of all prepared samples were investigated using energy dispersive X-ray spectroscopy, X-ray diffraction, UV-Vis spectroscopy, and electron spin resonance measurement. The results show that the anatase structure from TiO₂ and hexagonal wurtzite from ZnO remained unchanged with the incorporation of the Mn dopant. The grain size of the corresponding TiO₂ and ZnO slightly decreased after Mn incorporation, and the band gap energies of TiO₂ and ZnO nanoparticles decreased after Mn doping. The electron spin resonance measurement confirmed the existence of oxygen vacancy from the TiO₂ and ZnO lattice and increased with the incorporation of the Mn ion. To investigate the potential applications of the samples, the photocatalytic activity of the samples was evaluated to determine the degradation of malachite green from the aqueous solutions under UV light irradiations.

1. Introduction
Semiconductor materials have been widely investigated in many applications such as electronic, environmental, and energy applications [1,2]. Therefore, the development of semiconductors has become an important issue to improve their physical properties. TiO₂ and ZnO are the most investigated semiconductors for various applications due to their low cost and easy production [3,4]. ZnO and TiO₂ are the n-type semiconductor materials with a band gap energy around 3.2–3.4 eV [5,6]. Due to their interesting properties, ZnO and TiO₂ semiconductors have been widely used as photocatalysts, sensors, and other components [7,8]. However, modification of ZnO and TiO₂ to improve their physical properties such as structural and optical properties is challenging.

Manganese (Mn) incorporation/doped semiconductor is one of the solutions to improve the physical properties of the semiconductors. Several reports have suggested that Mn doped semiconductors could modify the optical and structural properties. For example, Ganesh et al. [9] studied Mn doped ZnO nanoparticles fabricated by hydrothermal method and found that the optical characteristics of Mn doped ZnO nanoparticles shifted to a higher wavelength and that the color of the nanoparticles changed from white to yellow. Viswanatha et al. [10] also reported the formation of Mn doped ZnO nanoparticles fabricated by a colloidal method and found that the optical characteristics of ZnO nanoparticles shifted to a lower wavelength. In addition, the shifted absorbance ability of Mn doped ZnO compared to the absorbance ability of ZnO nanoparticles is due to the quantum confinement effects.

Based on the presented explanation, this study compares the effect of Mn on the optical and the structural properties of ZnO and TiO₂ nanoparticles. Both samples were prepared by the co-precipitation method. The physical properties of all the fabricated samples are characterized using X-
ray diffraction (XRD), energy dispersive x-ray (EDX) spectroscopy, UV-Vis diffuse reflectance spectroscopy, and electron spin resonance (ESR). The photocatalytic activity of the both samples was also evaluated to investigate their potential applications for wastewater applications.

2. Experimental details
Several materials can be used without further purification, which include zinc (II) sulfate (ZnSO₄·7H₂O, 99%, Merck), manganese nitrate [Mn (NO₃)₂, Merck], and titanium chloride (TiCl₃, 99%, Merck). The required degree of Mn doping is obtained by mixing ZnSO₄·7H₂O and TiCl₃ in distilled water with Mn(NO₃). These solutions were designated as solutions A and B. Solutions A and B were accommodated in an ultrasonic cleaner for approximately 120 min and was operated at a frequency of approximately 57 kHz. Further, approximately 44 mmol NaOH was added to approximately 440 mL deionized water for obtaining a new solution, i.e., Solution C. Then sonication was applied. Further, Solution A was magnetically stirred at normal room temperature using a magnetic mixer, and Solution C was added to it till a pH of 12 was obtained. Subsequently, the solution was magnetically stirred for approximately 30 min; then it was left at normal room temperature for approximately 18 h. Centrifugal technique and washing were attempted to eliminate the unwanted residuals. Washing may be performed several times as per the requirement. Ethanol and distilled water were generally used for washing. Finally, the product was dried at 200 °C for approximately 60 min in a vacuum oven.

X-ray diffractometer was used to analyze the structural characteristics of the product. The Philips PW1710 model of X-Ray Diffractometer was used in the experiment along with monochromatic radiations of Cu-Kα having a wavelength of approximately 1.5406 Å and was operated at a voltage of 40 kV and a current of 20 mA, when 2θ = 10°–80°. Silicon powder is used to calibrate the diffractometer. The JCPDS data were used to compare and verify the patterns of X-ray diffraction of nanoparticles. Diffuse reflectance spectroscopy was applied for analyzing the optical performance and properties of the product. All the spectra for analysis were approximately 250–800 nm and a Shimadzu UV-Vis spectrophotometer, which was embedded with an integrating spherical attachment and enabled with the spectrolon reflectance standard, was used. All the experimental measurements of ESR were obtained for 0–71 T field. Electron-scanning-based EDX was used for analyzing the composition of the samples.

The photocatalytic activity is performed on the degradation of malachite green from the aqueous solution. Typically, 0.3 g of the catalyst was used to dissolve in 100 mL of the aqueous MB solution (20 mg/L). The photocatalytic process was noticed in a cylindrical glass vessel equipped with two UV-C lamps of 40-W and a magnetic mixer. The degradation of methylene blue was then monitored by UV-Vis spectroscopy. and the quantitative analysis of the photocatalytic experiment were calculated using the following equations:

\[
\text{Decolorization: } \frac{C_0}{C_t} \times 100 \% \\
\text{% Degradation: } \frac{C_0 - C_t}{C_0} \times 100 \%
\]

where \(C_0\) and \(C_t\) are the initial dye concentration the dye concentration after time \(t\), respectively

3. Results and discussion
Elemental analyses of Mn doped TiO₂ and ZnO nanoparticles investigated by EDX measurement are plotted in figure 1. As a comparison, the variation of EDX spectra of TiO₂ and ZnO are compared and plotted in the figure. This figure shows that the EDX spectrum of TiO₂ has several peaks at 4.48, 4.96, and 0.49 keV that correspond to the existence of Ti and O atoms. While ZnO has several peaks at 1.00 keV and 8.54 keV that correspond to the Zn atom, the O atom was also detected at 0.49 keV. The Mn atom was also detected by EDX measurement for both the samples, i.e., Mn doped ZnO and Mn doped TiO₂ samples at 5.78 and 6.41 keV, respectively. After integrating the whole EDX spectrum of Mn doped ZnO and Mn doped TiO₂, the results showed that the Mn dopant concentration was about 6 % for both samples. There were no undesired materials detected, indicating the existence of Mn doped ZnO and Mn doped TiO₂ nanoparticles.

The X-ray diffraction analysis of Mn doped TiO₂ and ZnO are plotted in figure 2. The figure shows that TiO₂ has several diffraction peaks at \(2\theta \approx 25.3^\circ, 37^\circ, 37.73^\circ, 38.54^\circ, 48^\circ, 53.84^\circ, 55^\circ, 62.02^\circ, 62.62^\circ, 68.7^\circ, 70.2^\circ, 74.94^\circ,\) and \(76.06^\circ\), corresponding to the plane of the anatase structure. In
Table 1. Grain size and lattice parameters of ZnO, TiO₂, and Mn doped ZnO and Mn doped TiO₂

| Sample          | Lattice parameters | Grain size |
|-----------------|--------------------|------------|
|                 | ZnO a=b c         | TiO₂ a=b c | ZnO | TiO₂ |
| ZnO             | 3.254 5.215        |            | - 20 |
| Mn doped ZnO    | 3.252 5.214        |            | - 16 |
| TiO₂            | -                  | -          | - 63 |
| Mn doped TiO₂   | -                  | -          | - 62 |

Figure 1. EDX intensity spectra of (a) ZnO and ZnO doped with Mn and (b) TiO₂ and TiO₂ doped with Mn

Figure 2. X-ray diffraction spectra of (a) the ZnO nanoparticles doped with Mn and (b) the TiO₂ nanoparticles doped with Mn

addition, the diffraction peaks of ZnO were detected at 2θ ≈ 31.72°, 34.38°, 36.15°, 47.50°, 47.50°, 56.64°, 62.83°, 67.99°, and 68.88°, corresponding to the hexagonal wurtzite of ZnO. After doping with the Mn atom, the diffraction peak of TiO₂ and ZnO remained unchanged. No undesired peaks were detected, indicating that the samples were successfully formed. The lattice parameters of TiO₂ and ZnO and Mn doped ZnO and TiO₂ are plotted in table 1, and the table shows that the correspond lattice parameters of TiO₂ and ZnO slightly changed after Mn incorporation. This could be due to the
Table 2. Band gap energy of ZnO, TiO$_2$, and Mn doped ZnO and Mn doped TiO$_2$.

| Sample             | Band Gap (eV) |
|--------------------|---------------|
| ZnO                | 3.37          |
| Mn doped ZnO       | 3.30          |
| TiO$_2$            | 3.20          |
| Mn doped TiO$_2$   | 3.11          |

Figure 3. UV-Vis spectra of (a) ZnO and Mn doped ZnO. (b) TiO$_2$ and Mn doped TiO$_2$.

substitution of Ti$^{4+}$ ion and Zn$^{2+}$ with Mn$^{2+}$. This happens because the ionic radii of Mn ions (0.80 Å) are higher than the radii of Zn ions (0.74 Å) resulting in the replacement of Zn ions by Mn ions. In contrast, the increased lattice parameters of Mn doped TiO$_2$ is due to the substitution of Mn$_{4+}$ having an ionic radius of 0.80 Å for Ti$^{4+}$ with an ionic radius of 0.60 Å. The grain size TiO$_2$ and ZnO and Mn doped ZnO and TiO$_2$ were calculated using the Williamson–Hall plots from the different peaks:

$$\beta_{hkl} = \frac{k\lambda}{D} + 4\varepsilon \sin(\theta)$$  \hspace{1cm} (3)

where $\beta_{hkl}$, $D$, $k$, $\lambda$, and $\varepsilon$ are the full width at half maximum (FWHM), average crystallite size, shape factor, wavelength of the Cu–K$_{α}$ radiation, and microstrain parameter, respectively. Shape factor $k$ is considered as 0.9 for this study. The linear plot of the W-H plot equations is plotted in figure 3, and the figure shows that both samples have good coefficient correlation. The grain size values of the samples were taken from the intercepts of the W-H plot analysis, and the values are presented in table 1. The table shows that the grain sizes of ZnO and TiO$_2$ are around 20 and 60 nm, respectively; however, after Mn doping, the grain size values slightly decreased to 16 and 32 nm, respectively. The reduction of grain size value is due to the existence of Mn atom in the structural of ZnO and TiO$_2$, preventing the crystal growth of ZnO and TiO$_2$ nanoparticles. The substitution of Mn ions into the ZnO and TiO$_2$ lattices can produce few defects. Thus, change in defect concentration can change the rate of crystal growth.

The UV-Vis diffuse reflectance spectra of all prepared samples are plotted in figure 3. Figure 3a shows that the reflectance ability in the range of visible light (FWHM) of ZnO and TiO$_2$ significantly decreased with the incorporation of the Mn atom. The decreased reflectance ability of Mn doped ZnO could correlate with the improved absorbance ability of Mn doped ZnO and Mn doped TiO$_2$ and the improved absorption ability in the visible light region of Mn doped ZnO and Mn doped TiO$_2$. The band gap energy of the Mn doped TiO$_2$ and Mn doped ZnO samples were calculated using Kubelka-Munk analysis.

$$F(R) = ((1 - 2R)^2)/2R$$ \hspace{1cm} (4)

where R represents the reflectance spectra of the samples. The band gap energy was obtained by
extrapolating $F(R) = 0$ vs energy. The extrapolating results are presented in table 2. The table shows that the band gap energies of Mn doped ZnO and Mn doped TiO$_2$ were lower than pure ZnO and TiO$_2$ nanoparticles, clearly indicating the existence of additional energy levels beneath the conduction bands of ZnO and TiO$_2$ after Mn incorporation.

To detect additional energy level below the conduction band of ZnO and TiO$_2$, the ESR measurement is a suitable measurement to detect impurities in the samples. The ESR spectra of Mn doped ZnO and Mn doped TiO$_2$ are plotted in figure 4. The figure shows that the Mn doped ZnO samples showed a senarius line resulting from isolated Mn$^{2+}$ ions in the wurtzite ZnO crystal field, revealing that Mn$^{2+}$ ions had started to replace Zn$^{2+}$ lattice. The ESR spectra of Mn doped TiO$_2$ shows several signals that can be attributed to the existence of oxygen vacancies and Ti$^{3+}$. The hyperfine structure from Mn$^{2+}$ is seen in the range of 3415 Gauss and 3359 Gauss [11,12].

In addition, the existence of Mn$^{2+}$ and oxygen vacancies can be confirmed by ESR measurement that indicate that the UV-Vis explanation is reasonable for the band gap narrowing of the Mn doped ZnO and Mn doped TiO$_2$ samples.

The photocatalytic activity of Mn doped TiO$_2$ and Mn doped ZnO nanoparticles is investigated on the degradation of malachite green, as can be seen in figure 5. The figure shows that the absorbance spectra of malachite green gradually decreased with increased irradiation time. This is due to the removal of malachite green from the aqueous solution through a photocatalytic process by using a
photocatalyst under UV light irradiations. The quantitative analysis of the photocatalytic activity of Mn doped TiO$_2$ and Mn doped ZnO are plotted in figure 6, and the figure shows that the photocatalytic activities of Mn doped TiO$_2$ and Mn doped ZnO possess good photocatalytic performance with degradation abilities approximately 75 and 68 \% for Mn doped ZnO and Mn doped TiO$_2$, respectively. Consequently, the Mn doped TiO$_2$ and Mn doped ZnO nanoparticles possess potential applications for wastewater removal through the photocatalytic process.

4. Conclusions
Mn doped TiO$_2$ and Mn doped ZnO have been successfully analyzed using the co-precipitation method. The wurtzite structure from ZnO and anatase structure of TiO$_2$ confirm the successful incorporation of Mn atom in the structure of ZnO and TiO$_2$ nanoparticles. Furthermore, the reflectance ability of Mn doped ZnO as well as Mn doped TiO$_2$ decreased compare to ZnO and TiO$_2$ nanoparticles. The band gap energy of Mn doped ZnO and Mn doped TiO$_2$ are smaller compared to pure ZnO and TiO$_2$ nanoparticles. The decreased band gap energy is due to the existence of oxygen vacancies and Mn$^{2+}$, and they were successfully detected by ESR measurement. The photocatalytic activities of Mn doped TiO$_2$ and Mn doped ZnO nanoparticles show good photocatalytic performance on the decay of malachite green from the aqueous solution, indicating that both samples can be used for wastewater removal applications.

References
[1] Tripathy S K and Pattanaik A 2016 Opt. Mater. 53 123–33
[2] Di J, Xia J, Li H, Guo S and Dai S 2017 Nano Energy 41 172–92
[3] Huang X, Zheng X, Xu Z and Yi C 2017 Int. J. Pharm. 534 190–4
[4] Haider A J, AL-Anbari R H, Kadhim G R and Salame C T 2017 Energy Procedia 119 332–45
[5] Samsudin E M and Hamid S B A 2017 Appl. Surf. Sci. 391 326–36
[6] Zheng W, Ding R, Yan X and He G 2017 Mater. Lett. 201 85–8
[7] Davari N, Farhadian M, Nazar A R S and Homayoonfal M 2017 J. Environ. Chem. Eng. 5 5707–20
[8] Firdaus C C M, Rizam M S B S, M.Rusopa and Hidayah S R 2012 Procedia Eng. 41 1367–73
[9] Ganesh R S et al. 2017 J. Alloys Compd. 721 182–90
[10] Viswanatha R et al. 2004 J. Phys. Chem. 108 6303–10
[11] Mhlongo G G et al. 2016 Appl. Surf. Sci. 390 804–15
[12] Zhang J, Jin J, Feng C, Yu L, Zhang J and Zhang Z 2011 J. Solid State Chem. 184 3066–73