Photocatalytic activity of transition metals (Mn, Fe, Ag and Ni doped ZnO) nanomaterials synthesised via sol-gel method: Active sites over band gap

A K A Darman\textsuperscript{1,3}, M L Ibrahim\textsuperscript{1,3}, H A Rafaie\textsuperscript{2}, M S Mastuli\textsuperscript{1,3} and M F Kasim*\textsuperscript{1,3}

\textsuperscript{1}Centre for Nanomaterials Research, Institute of Science, Level 3 Block C, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia
\textsuperscript{2}School of Physics and Materials studies, Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia
\textsuperscript{3}School of Chemistry and Environment, Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia
muhdffir@uitm.edu.my

Abstract. Dopants with varied stoichiometry values were examined to determine their performances on photocatalysis. The sol-gel method was successfully synthesised using transition metals, namely manganese (Mn), iron (Fe), silver (Ag) and nickel (Ni), as dopants in ZnO nanostructure. Zn\(_{1-x}\)Mn\(_x\)O, Zn\(_{1-x}\)Fe\(_x\)O, Zn\(_{1-x}\)Ag\(_x\)O and Zn\(_{1-x}\)Ni\(_x\)O (x=10\%) were characterised by using X-ray diffraction (XRD), BET surface area analysis, temperature-programmed desorption of carbon dioxide (TPD-CO\(_2\)) and UV-Vis spectrophotometer. A phase study on Mn- and Fe-doped ZnO nanoparticles confirmed that both the dopants experienced exceptional crystallinity with single-phase but Ag- and Ni-produced a multi-phases structures. Active sites of catalyst is proven to be an additional factor contributing towards photocatalysis in this work besides band gap and surface area. Temperature-programmed desorption of carbon dioxide (TPD-CO\(_2\)) showed that the incorporation of Ag into ZnO lattice has enhanced the number of active sites on the surface of the catalyst whereas incorporation of Mn, Fe and Ni in ZnO has reduced it as compared to pure ZnO. Photocatalytic degradation of methyl orange for all stoichiometry of Ag-doped ZnO nanoparticles resulted in lower degradation time. Interestingly, 10\% of Ag-doped ZnO achieved the highest degradation rate as much as 97.47 \% at 160 minutes, hence emerging as the best amongst all other compositions.

1. Introduction

These photocatalysis is the mechanism by which light irradiation is used to enable the catalyst for chemical reactions to be initiated. This process helps to remove organic compounds on a daily basis and is helpful to the treatment system of wastewater. Industrial effluent produces colorants such as textiles, ceramics, paints, and pulp & paper industries that increase the level of toxicity in water streams. Extensive photocatalytic research studies have covered a number of topics, including the development of photocatalysts, ways to improve the performance of photodegradation, critical variables associated with photocatalytic efficiency, as well as advancement and photocorrosion [1]. The broad range of photocatalysis offers a general solution to the pressing problem of water pollution and offers a
contrabalance to environmental safety [2]. The picture has been extensively used for its image degradation function, including zinc oxide (ZnO), titanium dioxide (TiO2), and iron (II) oxide. High photocatalytic activity is achieved by oxide based materials, thus enhancing photocatalytic effects [3]. The association with band gap energy is another problem of photocatalytic action. The importance of band gaps generally has an important role to influence semiconductor output. In order to produce photoexcitement, ZnO has a large and direct band gap, which requires a huge amount of energy of the beam (photons). The recombination phenomenon which results in dissipation of absorbed energy in the shape of lattice vibration (heat) and photon generation (light) means that some carriers cannot participate in photocatalytic activities. ZnO performance as a photocatalyst is degraded by the strong recombination of photogenerated electrons and holes pair. There is thus a need to emphasize the need to incorporate dopants as electron scavengers to overcome this obstacle in the efficient transport and separation of charge carriers in photocatalyst [4]. Doping contributes specifically, by increasing the band gap by three, (i) encouraging adsorption, (ii) enhancing ZnO conductance and carrier flexibility, and (iii) altering ZnO’s steering and valence band position. Many ZnO semiconductor components have attracted more attention among many scientists, due to the increased amount of charge trap, which decreases the volume recombination, and also more efficiency in the separation of photogenerated electrons and holes [4]–[6].

It has been stated that the transition metal dopants (Mn, Fe, Ag, Ni) work well for improving photocatalytic efficiency and creating a synergistic effect [7]. Nevertheless, no important study was conducted on changes in the band gap in light of photocatalytic activity. In addition, Pant et al.’s work on band-gap power, expressing Ag-doped ZnO improved photocatalytic activity successfully, is not in detail [5]. Sonal et al. revealed that Ni in ZnO/carbon-nanospheres were better photocatalyzed and yet no specific work on the analysis of band-gap [6]. Meanwhile for Mn/ZnO, successful work has been achieved by Aehouri et al. in decreasing the band gap value from 3.06 eV to 2.83 eV but doesn’t correlate the work with photocatalytic activity of Mn [8]. Similarly to Fe/ZnO, Khayatian et al. showed there is an increment when doping with Fe, yet no relationship study for band gap and photocatalysis [9]. This research therefore ties a valid theory with photocatalysis-related circumstances of band gap.

Different techniques such as sol-gel [10]–[12], hydrothermal [13]–[15], combustion [16]–[18] and chemical vapor deposition [19], [20] have been used for the preparation and processing of ZnO-doped synthesis. The route of synthesis is important because photocatalytic output varies from one path to another. This analysis uses undoped ZnO, Zn$_x$Mn$_{1-x}$O, Zn$_x$Fe$_{1-x}$O, Zn$_x$Ag$_{1-x}$O and Zn$_{1-x}$Ni$_x$O (x= 10 %). To date, several studies have successfully investigated photocatalytic dopants [5]–[9], [21]–[22], but none documented the relationship between band gap and photocatalytic. For example, Ahmad et al. conducted an analysis of the band gap, the particle size of the photocatalyst, photocatalyst surface and photocatalytic operation, showing that the greater the band gap is. This seems to be the enhancing element of photocatalytic action [7]. The purpose of this study in the present paper is therefore to bridge the information gap between fundamental work and work on application which attempts to overcome the band gap that had not been addressed much in previous studies [5]–[9], [21]–[22]. In the present work, XRD, BET Surface Analysis, TPD-CO2 and UV-Vis Spectrophotometer characterized the synthesized doped nanocatalysts. The photodegradation investigation was performed under UV light.

2. Experimental

2.1. Materials

Zinc acetate dihydrate was purchased from R&M chemicals with 99.5% purity. Manganese (II) acetate 99%, Ferum (II) acetate 95%, Silver (II) acetate 99% and Nickel (II) acetate 98% were purchased from Aldrich. These starting materials were mixed with absolute ethanol AnapuR.

2.2. Photocatalytic activity

Undoped and 10% of M-/ZnO (M= Mn, Fe, Ag and Ni) nanoparticles were synthesised under mild sol-gel treatment method. Zinc acetate dihydrate and Manganese (II) acetate tetrahydrate/ Ferum (II)
acetate/Silver acetate/Nickel (II) acetate tetrahydrate were dissolved under absolute ethanol and was stirred for 2 hours to gain a homogenous mixture. Base (ammonium hydroxide) was applied to increase the pH value to 9 and was accompanied by a heating process at 100 °C. Slow drying was done and grey precursors were obtained within 24 hours. STA (Jupiter STA449-F5) was further used to analyze nanoparticle specimens. Both TGA and DSC provided the most appropriate temperature to continue with the annealing process. For 3 hours, the precursors are cured at 400 °C. Next, structural crystallinity tests were performed following the annealing process using XRD (PANalytical) X’pert Pro powder diffraction equipment. The band gap test, which describes the properties of light absorption, was performed under reflectance (% R) mode using the Perkin Elmer Lambda 950 UV-Vis-NIR spectrophotometer. BELSORP-mini II Instrument by BEL Japan Inc. has measured the surface area. Under the plot of Brunauer-Emmett-Teller (BET), the different surface areas of undoped, Mn-, Fe-, Ag- and Ni / ZnO are plotted. Measurement of active sites was determined using TPD-CO₂. 

2.3. Photocatalytic activity

The photocatalytic activity of M-/ZnO nanoparticles was determined by the determination of the decomposition of methyl orange at constant room temperature at each interval. The catalyst loading was 100 mg of M-/ZnO catalyst, with an initial concentration of 10 ppm in a medium beaker containing 100 mL of methyl orange solution. UV-light radiation was turned on at 352 nm wavelength and 8 W wavelength. The dye solution was obtained at every 40-minute interval. The photocatalytic analysis was performed using UV-Vis spectrophotometer under absorbance, (A), mode. The peak of absorption of methyl orange was estimated at 464 nm. Efficiency of photodegradation (percent) was measured with respect to the total photodegradation at each interval. The constant frequency of photodegradation, k, has been determined for all samples. Before photodegradation, absorption regulated graph was created by excluding UV-light irradiation.

3. Results and discussion

3.1. Phase study

Figure 1 showed the pattern of XRD for M-/ZnO nanostructures varying from 20° to 90°. Excellent crystallinity was achieved as the diffracted peaks showed a good match with the ICDD reference number 01-089-0510 of ZnO wurtzite hexagonal with the P63mc space band. On Mn-and Fe/ZnO, there were no additional diffraction peaks noted as it is well-slotted and completely replaced between the ZnO structures boundaries. Because the ionic radius of Mn²⁺ (0.66 Å) and Fe²⁺ (0.70 Å) is smaller than that of Zn²⁺ (0.74 Å), the dopant atoms integrated in the ZnO lattices did not alter the overall crystal structure.

As for the Ag/ZnO, diffraction peaks of Ag metal are observed in accordance with the standard Ag ICDD reference number 01-087-0717 at (111), (200), (220), and (311) crystal plane. This phenomenon is due to the immense ionic size difference in the ZnO system between Ag⁺ ions (1.15 Å) and Zn²⁺ ions. The presence of Ag metal seemed to have an influence on the manufacture of ZnO [23], [24]. While, the diffraction peak found on Ni/ZnO consisting of NiO and Ni metals at (200) and (111), Ni ICDD reference numbers 01-073-1519 and 00-001-1266, respectively. At 10 % Ni doping, phases added has weakened the bonding of Zn-O connections [26].

No shifts are found in the peak positions for Ag and Ni samples based on the XRD trend. The diffraction peaks for both Ag and Ni dopants showed weaker intensity as compared to undoped ZnO which indicates that metal atoms are not well-slotted into the lattice of ZnO, but squeezed in the grain boundaries of ZnO crystallites [25], [26]. Therefore, the Ag- and Ni/ZnO phenomenon was referred to as interstitial doping.
3.2. Band gap study

Figure 2(a) displayed the annealed test optical band gap at 400 °C M-/ZnO. Data absorption edges provide information related to the excitonic and inter-transition of nanomaterials [27], [28]. The change from UV absorption peak spectra observed on the chart from 370 nm to 410 nm is primarily due to the varying sizes of nanomaterials. Reflectance spectra of ZnO is higher than other dopant elements throughout the visible region. Decrease in reflectance spectra may torch better photocatalyst, hence producing better photocatalytic activity theoretically. This decrease is due to various sub-levels through the bandgap of ZnO, giving chances for band gap decrement. There are no fluorescence signal observed for undoped and M-/ZnO after 380 nm indicates the presence of carrier traps within the nanoparticles [10]. Higher particle size of nanocatalyst produces lower surface area, resulting in lower energy value of the band gap, according to Ahmad et al., (2015). Thus, different nanocatalyst sizes can cause the peak to move slightly [22], [28]. The Tauc relationship was also plotted on the basis of the edge of absorption deduced from the spectra of reflection. The Tauc relation was applied via equation below:

\[
(\alpha h\nu) = C(h\nu - E_g)^n
\]  

From the Tauc relationship, \( \alpha \) represents the material's absorption coefficient, \( h \) denotes Planck's constant, \( \nu \) reflects the light rate, \( C \) is the proportionality constant, \( E_g \) refers to the band gap power, and \( n= \frac{1}{2} \) (for materials in direct transition mode), as ZnO is known as a direct band gap semiconductor [29]-[31]. In this analysis, the absorption coefficient was calculated by:
\[
\alpha = k \ln\left(\frac{R_{\text{max}} - R_{\text{min}}}{R - R_{\text{min}}}\right) \quad (2)
\]

\(k\) is a constant dependent on the absorption coefficient, \(R_{\text{max}}\) stands for total reflection, and \(R_{\text{min}}\) corresponds to minimal reflection. Equation (1) and (2) give the following results:

\[
(\alpha h\nu)^2 = C' (h\nu - E_g) \quad (3)
\]

Extrapolation was obtained from the \((\alpha h\nu)^2\) graph against \(h\nu\), while band gap energy was measured once it reached the x-axis, abscissa line. For M-\(\text{ZnO}\), respectively, the Tauc plot graph and the extrapolation are shown in Figure 2(b). The values of the band gap are shown in Table 1. Change of absorption edge and band gap occurred at interstitial doping is due to metal substitution at the \(\text{Zn}^{2+}\) site. For example, Ni content in the \(\text{ZnO}\) system resulted in the presence of the NiO phase due to incomplete substitution. This situation weakened \(\text{Zn-O}\) bonding, but activated Ni-O growth \cite{26}, \cite{32}. The improvements observed in the Ag- and Ni-doped \(\text{ZnO}\) band gap values are due to grain size, structural factor, and concentration of carrier \cite{33}, \cite{34}. Dopants such as Mn, Ag and Ni have larger band gap than undoped \(\text{ZnO}\) because ions form each representative dopant replaced \(\text{Zn}^{2+}\) lattice and contributed to free electrons which eventually makes Fermi level going towards or be as same level as conduction band \cite{11}.

The band gap has a major role to play in evaluating the efficiency of photocatalysis. This research proves that other factors, as described above, may reduce the band gap as the main factor for photodegradation of methyl orange, as elaborated in the following section.

**Table 1.** Band gap energy values of undoped and M-\(\text{ZnO}\) with different stoichiometry.

| Sample       | Band gap energy value (eV) |
|--------------|----------------------------|
| Undoped \(\text{ZnO}\) | 3.29                      |
| 10 \% Mn/\(\text{ZnO}\) | 3.33                      |
| 10 \% Fe/\(\text{ZnO}\) | 3.27                      |
| 10 \% Ag/\(\text{ZnO}\) | 3.31                      |
| 10 \% Ni/\(\text{ZnO}\) | 3.35                      |

**Figure 2.** The result of (a) UV-Visible spectra and (b) Tauc plots of M-\(\text{ZnO}\) on each dopant.

### 3.3. Surface area analysis

Table 2 shows the distribution on undoped and M-\(\text{ZnO}\) of \(\text{N}_2\) adsorption-desorption and pore length. It is possible to classify all adsorption isotherms as Type II based on the International Union of Pure and Applied Chemistry (IUPAC) classification standard. The porosity reveals its macroporous nature under
Type II conditions. Building Brunauer-Emmett-Teller (BET) plot calculated the approximate surface area, maximum pore density and average pore diameter of undoped and M-/ZnO. Table 2 tabulates the textural properties on each dopant. 10 % Ag/ZnO appeared to result in the smallest specific surface area, and followed by undoped, Mn-, Fe- and Ni/ZnO. As for Ni / ZnO, the smallest size of crystallite was the highest specific area of the layer. High surface area is expected to result in strong photocatalytic behavior in principle. Nonetheless, compared to either undoped or Ag/ZnO, Mn-, Fe- and Ni/ZnO did not generate better photocatalytic activity. In this case, the Mn-, Fe- and Ni / ZnO sites are thought to be inactive against photocatalytic reaction [35], [36].

| Sample      | a$_{BET}$ (m$^2$g$^{-1}$) | Total pore volume (cm$^3$g$^{-1}$) | Average pore diameter (nm) |
|-------------|---------------------------|-----------------------------------|---------------------------|
| Undoped ZnO | 11.671                    | 0.1618                            | 55.448                    |
| 10 % Mn/ZnO | 13.562                    | 0.1257                            | 37.063                    |
| 10 % Fe/ZnO | 13.621                    | 0.0835                            | 24.517                    |
| 10 % Ag/ZnO | 9.7801                    | 0.1363                            | 55.736                    |
| 10 % Ni/ZnO | 14.207                    | 0.1958                            | 56.754                    |

3.4. Active sites measurement
TPD profiles represented the interaction between CO$_2$ molecules and Table 3 tabulated photocatalyst surfaces. CO$_2$ desorption occurred at temperatures ranging from 300 °C to 550 °C, demonstrating that all specimens were high basic centers. At temperatures above 350 °C, both undoped ZnO and Ag/ZnO showed a strong desorption maximum. 10 % Ag/ZnO had the highest total volume of basicity (see Figure 3), in which the photocatalyst surface had the highest active sites. Ag/ZnO is therefore a likely place to initiate a good photocatalytic performance compared to Mn-, Fe- and Ni/ZnO. In Mn-, Fe- and Ni/ZnO, asymmetrical, low and decreasing desorption peak was noted due to diffusion limitation and decomposition of species of carbonates. Limitation in diffusion caused by limited distribution of pores on pore volume and dopant Mn, Fe and Ni diameter resulted in low total active site volumes. Although the surface area of Mn-, Fe- and Ni/ZnO (see Table 2) has a slight resemblance to surface area analysis, the sites in them are thought to be less active. Therefore, the photocatalyst surface coverage of reactive adsorbed species is smaller, leading to inadequate photocatalytic efficiency [37]-[39].
### Figure 3. CO$_2$ – TPD profiles of (a) undoped ZnO (b) 10% Mn/ZnO (c) 10% Fe/ZnO (d) 10% Ag/ZnO and (e) 10% Ni/ZnO nanomaterials.

### Table 3. Basic sites of undoped and M-/ZnO determined by TPD-CO$_2$.

| Sample          | Temperature (℃) | Amount of CO$_2$ desorbed (µmol/g) | Total amount of basicity (µmol/g) |
|-----------------|-----------------|------------------------------------|----------------------------------|
| Undoped ZnO     | 465             | 57.92                              | 119.77                           |
|                 | 754             | 61.85                              |                                  |
| 10% Mn/ZnO      | 446             | 39.39                              | 58.02                            |
|                 | 651             | 18.63                              |                                  |
| 10% Fe/ZnO      | 429             | 10.74                              | 58.34                            |
|                 | 649             | 47.60                              |                                  |
| 10% Ag/ZnO      | 140             | 19.35                              | 166.53                           |
|                 | 494             | 147.18                             |                                  |
| 10% Ni/ZnO      | 428             | 34.08                              | 61.38                            |
|                 | 599             | 27.30                              |                                  |

### 3.5. Photocatalytic activity

The photodegradation of undoped and M-/ZnO nanomaterials was calculated by evaluating each interval (40 minutes) under 352 nm 8W UV light irradiation of 10 ppm methyl orange aqueous solution. It is revealed, with UV light irradiation, the time-dependent absorbance spectra for undoped and M-/ZnO for 160 minutes from 350 nm to 550 nm. The characteristic value, $\lambda_{max}$, was at 464 nm for methyl orange based on the chart. After 160 minutes, undoped and Ag/ZnO showed promising photodegradation with complete clarity, while Mn-, Fe-and Ni/ZnO produced low photocatalytic efficiency.

Photodegradation efficiency (%) was calculated from the graph on the basis of the absorbance measured from each interval. The photocatalytic degradation efficiency is expressed in Equation 4, as follows:

$$\text{Photocatalytic degradation efficiency} (\%) = \left[ \frac{(C_0 - C)}{C_0} \right] \times 100 = \left[ \left( \frac{A_0 - A}{A_0} \right) \right] \times 100 \quad (4)$$

$C_0$ represents the initial concentration of dye from the formula, while $C$ denotes the concentration of dye in terms of time (minutes) at each interval. In the meantime, $A_0$ is the initial absorption, while $A$ corresponds to the absorption of methyl orange at each interval at a common absorption wavelength of 464 nm. [40], [41].

Figure 4(a) showed the undoped and M-/ZnO photocatalytic behavior that Ag/ZnO tends to be stronger than Mn-, Fe-and Ni/ZnO. 10% Ag/ZnO resulted in the highest efficiency of degradation with 97.47%. Meanwhile, Mn-, Fe-and Ni/ZnO reported low photocatalytic degradation efficiency. For 10%
of them with 5.48%, 12.31% and 13.44% respectively, no appreciable photodegradation efficiency was observed. The photodegradation rate constant, k, of undoped and M-/ZnO had been assessed using the kinetic model suggested by Langmuir-Hinshelwood, which is pseudo-first kinetics model of photocatalysis [42], as given in Equation 5 below:

$$\ln \left( \frac{C}{C_0} \right) = -kt$$  \hspace{0.5cm} (5)

From the formula, $C_0$ represents the initial methyl orange concentration, $C$ corresponds to the methyl orange concentration at each interval, and $t$ is the time of irradiation. The $\ln \left( C/C_0 \right)$ graph against $t$ shows a linear relationship in Figure 4(b), followed by kinetics of pseudo-first-order reaction. In Table 4 for undoped and M-/ZnO, the pseudo-first order frequency constant, $k$, and linear regression, $R^2$, are tabulated respectively. 10% of Ag content in ZnO gave the highest $k$ values amongst other dopants.

**Table 4. Photocatalytic performance of undoped and M-/ZnO nanoparticles.**

| Sample          | Percentage degradation, (%) after 160 minutes | Photodegradation rate constant, $(k, \text{min}^{-1})$ | $R^2$ | Band gap energy value $(eV)$ |
|-----------------|---------------------------------------------|------------------------------------------------------|-------|-----------------------------|
| Undoped ZnO     | 77.66                                      | 0.0088                                               | 0.9824| 3.29                        |
| 10 % Mn/ZnO     | 5.48                                       | 0.0004                                               | 0.9814| 3.33                        |
| 10 % Fe/ZnO     | 12.31                                      | 0.0007                                               | 0.9068| 3.27                        |
| 10 % Ag/ZnO     | 97.47                                      | 0.0233                                               | 0.9624| 3.31                        |
| 10 % Ni/ZnO     | 13.44                                      | 0.001                                                | 0.9702| 3.35                        |

**Figure 4.** The result of (a) photocatalytic degradation efficiency of M-/ZnO and (b) curves of $\ln \left( C/C_0 \right)$ vs time.

This research clearly shows that the quality of the M-/ZnO photocatalysis did not significantly affected band gaps. Band gap is the energy gap that represents the existence of photogenerated holes and excited electrons between the valence range and the conduction band. In general, the photocatalytic cycle (see Figure 10) occurs when the energy of a semiconductor, which is ZnO, is more than the origin. Electrons from the valence band (VB) are therefore excited to move to the conduction band (CB).

As an electron scavenger, the dopants (Mn/Fe/Ag/Ni) capture excited electron intercepting recombination of two holes, leading to an extended lifetime of the aroused electron. The reaction to $\text{H}_2\text{O}$ and exceptional oxidant ($\bullet\text{OH}, \bullet\text{O}_2^{-}$ and $\text{H}_2\text{O}_2$) molecules, which later degrades the dyes, is given greater time for excitable electrons and holes. The oxidant organism has the potential to degrade contaminants by breaking down organic bonds, including the degradation of aromatic rings of dye molecules and their reaction. [3], [43]. Generating more oxidizing organisms improves the efficiency of photocatalytic
activity. Ironically, due to the excellent result of the Ag/ZnO nanomaterials, the band gap is not a dominant factor in this work, as it turned out to be a good development in photocatalysis. The most extensive photocatalytic activity among other dopants was 10% of Ag material. Comparison between 10% Ag-, Mn-, Fe-and Ni/ZnO suggests that band gap is not the factor that controls photocatalytic activity in this work. 10% Fe/ZnO had a lower energy gap band value compared to 10% Ag/ZnO, but did not produce better photocatalytic efficiency. This shows that although 10% Fe/ZnO resulted in the smallest band gap, there was no interconnection with the output of photocatalysis which resulted in low photocatalytic activity. Theoretically, this condition is linked to Ag/ZnO due to the good quality of photodegradation, but not to Fe/ZnO, as well as to Mn- and Ni/ZnO. One of the main reasons for the superior photocatalytic quality in 10% Ag/ZnO is that active sites in Ag are available and the suspension has increased light penetration, indicating the plasmonic effect of Ag [44]. In addition, Mn-, Fe-and Ni/ZnO showed photo-phenomena because they showed lower photocatalytic activity because light penetration decreased. Limited access to the catalyst surface via agglomeration affects the adsorption efficiency. Based on the SEM images on Mn-, Fe-and Ni/ZnO, the inability to obtain long nanorods could be the explanation why the light could not penetrate more to its surface. [45], [46].

Dopants (Mn/Fe/Ag/Ni) had almost identical band gap energy values, but vary in terms of output. Therefore, photocatalytic activity cannot be mainly caused by the band gap. Other explanations for influencing the quality of photocatalytic may include surface area [47], [48], particle size [49], crystallinity, and quantum yield [50].

4. Conclusion

Ultimately, the process and performance of photocatalysis concludes fundamental band differences and application work. Synthesis on undoped and 10% M-/ZnO was performed using the modified sol-gel process. The association between band gap and photocatalytic behavior has been shown to be unfounded in this paperwork, as the band gap does not affect photocatalytic efficiency. Other considerations, such as active sites, surface area, quantum yield and crystalline volume, may be more suitable in substituting photocatalysis features. This paper showed that Ag/ZnO only performs better on photocatalysis, but this does not extend to Mn-, Fe-and Ni/ZnO, which equals the band gap value.

5. References

[1] Lee K M, Lai C W, Ngai K S and Juan J C 2016 Water Res. 88 428 - 448
[2] Qi K, Cheng B, Yu J and Ho W 2017 J. Alloys Compd. 727 792 - 820
[3] Rafaie H A, Nor R M, Azmina M S, Ramli N I T and Mohamed R 2017 J. Environ. Chem. Eng. 5(4) 3963–72
[4] Kang X, Liu S, Dai Z, He Y, Song X and Tan Z 2019 Catalysts 9(2) 191
[5] Pant B, Park M, Kim H Y and Park S J 2016 Synth. Met. 220 533–537
[6] Singhal S, Dixit S and Shukla A K 2018 Adv. Powder Technol. 29(12) 3483–92
[7] Türkylmaz Ş Ş, Güzey N and Özacar M 2017 J. Photoch. Photobio. A: Chem. 341 39–50
[8] Achioufi F, Corbel S, Balan L, Mozet K, Girot E, Medjahdi G, Said M B, Ghribi A and Schneider 2016 Mater. Design 101 309–316
[9] Khayatian A, Asgari V, Ramazani A, Akhtarianfar S F, Kashi M A and Safa S 2017 Mater. Res. Bull. 94 77–84
[10] Hasnidiwani J N, Azlina H N, Norita H, Bonnita N N, Ratim S and Ali E S 2016 Procedia Chem. 19 211–216
[11] Bekkari R, Ilaâbâb L, Boyer D, Mahiou R and Jaber B 2017 Mater. Sci. Semicon. Process. 71 181–187
[12] Mahdavi R and Ashrafl T S S 2017 Ultrasound. Sonochem. 39 504–510
[13] Kumaresan N, Ramamurthi K, Ramesh Babu R, Sethuraman K and Moorthy Babu S 2017 Appl. Surf. Sci. 418 138–146
[14] Ghoderao K P, Jamble S N and Kale R B 2018 Optik 156 758–771
[15] Bazazi S, Arsalani N, Khataee A and Tabrizi A G 2018 J. Ind. Eng. Chem. 62 265–272
[16] Sangeeta M, Karthik K V, Ravishankar R, Anantha Raju K S, Nagabhushana H, Jeetendra K, Vidyasagar S and Renuka L 2017 Synthesis of ZnO, MgO and ZnO/MgO by solution combustion method: Characterization and Photocatalytic studies Mater. Today: Proc., ed S. Bland (United Kingdom: Elsevier Ltd) vol 4 pp 11791–98
[17] Ajamein H, Haghighi M and Alaei S 2018 Mater. Res. Bull. 102 142–152
[18] Vasei H V, Masoudupanah S M, Adeli M and Aboutaleb M R 2018 Ceram. Int. 44(7) 7741–45
[19] Kumar S, Sahare P D and Kumar S 2018 Mater. Res. Bull. 105 237–245
[20] Narin P, Kutlu E, Atmaca G, Atilgan, A, Yildiz A and Lisesivdin S B 2018 Optik 168 86–91
[21] Siva Vijayakumar T, Karthikeyeni S, Vasanth S, Ganesh A, Bupesh G, Ramesh R, Manim and Subramanian P 2013 J. Nanosci. 2013 1–7
[22] Ajala F, Hamrouni A, Houas A, Lachheb H, Megna B, Palmisano L and Parrino F 2018 Appl. Surf. Sci. 445 376–382
[23] Thomas M A and Cui J B 2009 J. Vac. Sci. Technol. B.: Microelectron. Nanometer Struct. 27(3) 1673
[24] Wang L N, Zhou L, Zhou D, Yu Y, Luan Z Q, Tang D L, Zhu N, Gao Z H, Liu N and Hu, L Z 2017 Effect of annealing treatment on structure of Ag doped ZnO films deposited by thermal evaporation method IOP Conf. Mater. Sci. Eng. (United Kingdom: Institute of Physics) vol 213 p 12024
[25] Mohammad Kakhki R, Tayeebee R and Ahsani F 2017 J. Mater. Sci.: Mater. Electron 28(8) 5941–52
[26] Goswami N and Sahai A 2013 Mater. Res. Bull. 48(2) 346–351
[27] Singhal S, Kaur J, Namgyal T and Sharma R 2012 Physica B: Condens. Matter 407(8) 1223–26
[28] Kaneva N V and Dushkin C D 2011 Bulg. Chem. Commun. 43(2) 259–263
[29] Zhang T, Liang R, Dong L, Wang J, Xu J and Pan C 2015 Nano Res. 8(8) 2676–85
[30] Pearton S J, Norton D P, Ip K, Heo Y W and Steiner T 2005 Prog. Mater. Sci. 50 293 - 340
[31] Rusdi R, Rahman A A, Mohamed N S, Kamarudin N and Kamarulzaman N 2011 Powder Technol. 210(1) 18–22
[32] Zhao J, Wang L, Yan X, Yang Y, Lei Y, Zhou J, Huang Y, Gu Y and Zhang Y 2011 Mater. Res. Bull. 46(8) 1207–10
[33] Veldurthi N K, Jitta R R, Ravi G, Guje R, Velchuri R, Venkataswamy P and Vithal M 2016 ChemistrySelect 1(11) 2783–91
[34] Naveen Kumar S K, Gayithri K C and Kiran S 2015 Int. J. ChemTech Res. 7(2) 936–942
[35] Iwase M, Yamada, K, Kuri T, Ohtani B and Wakita H 2013 Appl. Catal. B.: Environ. 140–141 327–332
[36] Liao C Y, Wang H P and Lin H P 2013 Int. J. Photoenergy 2013 243160
[37] Guo J, Wang K and Xing Y 2017 Catal. Sci. Technol. 7(24) 6013–25
[38] Farabi M S A, Ibrahim M L, Rashid U and Taufiq-Yap Y H 2019 Energy Convers. Manag. 181 562–570
[39] Natesahawat S, Ohodnicki P R, Howard B H, Lekse J W, Baltrus J P and Matranga C 2013 Top. Catal. 56 1752–63
[40] Bai Y, Chen S, Lu L and Bao J 2013 Adv. Mater. Res. 602–604 169–173
[41] Aggarwal S 2016 Int. Res. J. Eng. Technol. 3 2–6
[42] Magalhães P, Andrade L., Nunes O C and Mendes A 2017 Rev. Adv. Mater. Sci. 51(2) 91–129
[43] Kumar R, Umar A, Kumar G, Akhtar M S, Wang Y and Kim S H 2015 Ceram. Int. 41(6) 7773–7782
[44] Zhao Z J, Hwang S H, Jeon S, Hwang B, Jung J Y, Lee J, Park S H and Jeong J H 2017 Sci. Rep. 7(1) 8915
[45] Mekasuwanandumrong O, Pawinrat P, Praserthdam P and Panpranot J 2010 Chem. Eng. J. 164(1) 77–84
[46] Grzechulska J and Morawski A W 2002 Appl. Catal. B.: Environ. 36(1) 45–51
[47] Kaur J and Singhal S 2014 Ceram. Int. 40(5) 7417–24
[48] Reinosa J J, Leret P, Álvarez-Docio C M, Del Campo A and Fernández J F 2016 Bol. Soc. Esp. Ceram. V. 55(2) 55–62
[49] Han R, Wang Y, Yu W, Zou W, Shi J and Liu H 2007 J. Hazard. Mater. 141(3) 713–718
[50] Lv J, Gong W, Huang K, Zhu J, Meng F, Song X and Sun Z 2011 Superlattice Microst. 50(2) 98–106

Acknowledgments

The authors wish to thank the internal grant agency funded by Universiti Teknologi MARA, Malaysia, under the UiTM Research Grant No. 600-IRMI/DANA KCM 5/3/LESTARI (103/2017). Special gratitude to Institute of Science, UiTM for provision of research instruments.