



SYNTHESIS, CHARACTERIZATION AND PHOTOCATALYTIC ACTIVITIES OF Mg-DOPED ZnO FOR DEGRADATION OF METHYLENE BLUE DYE UNDER UV LIGHT IRRADIATION

(Sintesis, Pencirian dan Aktiviti Fotokatalitik Mg di Dopkan dengan ZnO untuk Penguraian Pewarna Metilena Biru di Bawah Cahaya UV)

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Abstract

Heterogeneous photocatalysis is a viable treatment approach for removing organic dye compounds from textile wastewater, and ZnO-based photocatalysts is an appealing system to investigate. In this work, Mg-doped ZnO had been synthesized using modified sol-gel technique to evaluate the effect of different Mg molar concentrations towards the photocatalytic degradation performance of methylene blue (MB) dye. It had been characterized by X-ray diffraction (XRD), scanning electron microscope (SEM) and energy dispersive X-ray (EDS) analysis. According to XRD analysis, all samples showed a hexagonal wurtzite structure with average crystallite approximate sizes ranging between 74.82–81.64 nm. The SEM-EDS results demonstrated that the particle-like Mg-doped ZnO samples consist of elements Zn, O and Mg. The photocatalytic activity of the pure ZnO and Mg-doped ZnO was investigated through photodegradation of MB under ultraviolet radiation. The results showed that 1 mol% Mg-doped ZnO exhibited enhanced photocatalytic activity with a percentage of degradation of 89.54% and photodegradation rate constant, k of 0.0432 min^{-1} . Extended visible absorption, inhibition of photoexcited electron and hole recombination, and higher absorptivity of MB dye on the surface of Mg-doped ZnO photocatalyst might have contributed to the increased photocatalytic activity.

Keywords: magnesium, methylene blue, photocatalyst, photocatalytic, ZnO

Abstrak

Fotokatalisis heterogen adalah pendekatan rawatan yang terbaik untuk menghilangkan sebatian pewarna organik dari sisa buangan daripada industri tekstil, dan pemangkin berasaskan ZnO adalah sistem yang menarik untuk dikaji. Dalam penyelidikan ini, ZnO

yang didopkan dengan Mg telah disintesis menggunakan teknik sol-gel yang diubahsuai untuk menilai kesan kepekatan molar Mg yang berbeza terhadap prestasi penguraian pewarna metilena biru (MB) dan dicirikan dengan difraktogram (XRD), mikroskop elektron (SEM) dan sinar-X penyebaran tenaga (EDS). Dapatan dari analisis XRD, semua sampel menunjukkan struktur wurtzit heksagon dengan ukuran kristal kira-kira dalam julat 74.82-81.64 nm. Hasil SEM-EDS menunjukkan bahawa sampel ZnO yang didopkan dengan Mg terdiri daripada unsur Zn, O dan Mg. Aktiviti foto-penguraian ZnO dan Mg-doped ZnO dikaji dengan menjalankan pemerhatian penguraian larutan akues MB di bawah sinaran ultraviolet. Hasil kajian menunjukkan bahawa sampel 1 mol% ZnO yang didopkan dengan Mg menunjukkan peningkatan kecekapan fotomangkin dengan peratusan penguraian 89.54% dan kadar penguraian tetap, k 0.0432 min^{-1} . Penyerapan yang lebih meluas di kawasan cahaya nampak, penghambatan pengumpulan semula elektron dan lubang yang terangsang dengan foto, dan foto penguraian larutan akues metilena biru yang lebih tinggi pada permukaan fotokatalis ZnO yang didopkan dengan Mg mungkin menyumbang kepada peningkatan aktiviti fotokatalitik.

Kata kunci: magnesium, metilena biru, pemangkin, fotokatalitik, ZnO

Introduction

Environmental contamination has recently been recognized as one of the most serious challenges confronting modern society, with contamination of natural water supplies being the most serious, owing primarily to unmeasured population growth and increased industrial activity. The textile sector is one of the industrial processes that produces enormous amounts of wastewater. The dye effluent and colored discharge disposed into the water causes a significant impact on aquatic life and the environment due to their high stability under ambient conditions. As a result, researchers have focused on removing azo dyes from wastewater to comply with severe environmental requirements. Up to now, various treatment methods such as physical methods and chemical methods have been investigated to remove azo dyes [1]. Generally, the wastewater treatment process should be cost-effective and feasible for large-scale applications [2]. Overall, wastewater treatment might save a lot of water, and the treated water could be recycled or reused in industries like textiles and agriculture.

Recently, the utilization of oxide semiconductor nanomaterials as effective photocatalysts in wastewater treatment has become a subject of major concern [3]. Among the oxide semiconductors, zinc oxide (ZnO) is chosen as the semiconducting photocatalyst for pollution treatment in water because of its advantages such as easy to prepare, abundance, low cost, photostability, and large exciton binding energy of 60 MeV [4,5]. It also has a direct band gap energy at 3.37 eV at room temperature, making it a suitable candidate in absorbing UV-light as an excitation source

[6]. Several researchers reported that ZnO has good photocatalytic activity and shows the appropriate activity in the range of solar radiation [7–9]. Unfortunately, the industrial application of ZnO in the photocatalytic field has been impeded by two significant limitations which are (i) ZnO has a high recombination ratio of photo-induced electron-hole pairs, which limits its photocatalytic effectiveness; and (ii) ZnO largely absorbs ultraviolet light (380 nm) and can only be activated by visible light, restricting its photocatalytic activity in the visible light region [10,11]. Proposing effective techniques to improve visible light absorption and reduce recombination of photo-generated electron-hole pairs to achieve high-efficiency photocatalysts is therefore critical. One of the most common methods for achieving these goals is via metal doping [12,13]. Recently, efforts have been made to improve the photocatalytic activities of ZnO nanostructures by doping various chemical elements such as Al [14,15], Ni [16,17], Fe [18–20] and Ag [21,22]. Other than that, there is also a possibility that Mg-doping can also improve the photocatalytic activity of ZnO nanostructures by creating oxygen or zinc vacancies, due to the similar ionic radii of Zn^{2+} (0.060 nm) and Mg^{2+} (0.057 nm) [23–25].

In this work, Mg-doped ZnO at various concentration (1 – 10 mol%) were prepared through sol-gel method. The structural and morphological properties were characterized by XRD, and SEM equipped with EDS. Furthermore, the photocatalytic activities of pure ZnO and Mg-doped ZnO were also studied by degrading methylene blue (MB) in water.

Materials and Methods

Synthesis of photocatalyst

Commercial zinc oxide powder (denoted as pure ZnO) and magnesium nitrate ($\text{Mg}(\text{NO}_3)_2$) were purchased from Sigma-Aldrich with 99 % purity while hexamethylenetetramine (HMTA) was purchased from R&M chemicals with 99.5 % purity. For photocatalytic study {[7-(dimethylamino) phenothiazin-3-ylidene]-dimethylazanium;chloride} ($\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$) commonly known as methylene blue dye was used. The aqueous solutions were prepared with deionized water throughout the experimental process.

Mg-doped ZnO photocatalysts were synthesized using a modified sol-gel method as our previous work [26]. A mixture solution was prepared by dissolving the commercial ZnO powder and HMTA at constant molar concentration of 0.1 M in 100 ml of deionized water. For the synthesis of Mg-doped ZnO samples, magnesium nitrate ($\text{Mg}(\text{NO}_3)_2$) as a dopant source was added into the mixture solution at different mol % concentration of 1, 3, 5, 7 and 10 with respect to Zn, respectively. The mixed solution was magnetically stirred at 95 °C for 2 h to gain a homogenous mixture under vigorous stirring. The solution was aged for 24 h until a homogenous gel was formed. Next, the resulting gel was then collected and rinsed thoroughly using deionized water, followed by a drying process at 300 °C for 2 h. The pure ZnO and prepared Mg-doped ZnO photocatalysts at different doping concentration were characterized using several techniques. The crystal structures and phases of prepared nanoparticles were examined through X-ray diffraction (XRD) (PANalytical) X'pert Pro powder diffraction equipment using Cu-K α radiation ($k = 1.54056 \text{ \AA}$). The estimated crystallite size of pure ZnO and Mg-doped ZnO at various mol % concentration were obtained and calculated by using Scherer's as in equation (1) below [26]:

$$d = k\lambda \beta \cos\theta \quad (1)$$

Where k is the constant dependent on crystallite shape (0.94 nm), λ is the X-ray wavelength (1.54 Å), β is referring to the full width at the half max (FWHM) of the sample and θ is the Bragg's diffraction angle. The morphology of chosen samples was characterized by using field emission scanning electron microscopy (FE-SEM) (JEOL JSM-7600F). Subsequently, the samples were then used for photocatalytic degradation measurement.

Photodegradation evaluation

The photocatalytic activities of the pure ZnO and Mg-doped ZnO photocatalyst were evaluated by determining the degradation of methylene blue (MB) in aqueous solution on each interval at constant room temperature. The amount of catalyst used was 10 mg of pure ZnO and Mg-doped ZnO in a beaker containing 100 ml of MB solution with 5mg/L as the initial concentration. The UV-light with 365 nm wavelength with the definite power of 12 W, 230 Volts and 50 Hz frequency was used as a light source. Before switching on the lamp, the mixture was stirred in the dark for 30 min to reach adsorption-desorption equilibrium between the photocatalyst and MB. 5 ml of aliquots were extracted out at every 10 min interval and was monitored for 1 h. The schematic expression of experimental setup of photocatalytic measurement is shown in Figure 1. The photocatalytic analysis was performed using UV-Vis spectrophotometer under absorbance, (A), mode. The residual concentration of MB was measured at 664 nm using UV-vis spectrophotometer (Shidmadzu UV-1800UV). The percentage of degradation (%) was measured regarding the maximum photodegradation collected at each interval using the equation below:

$$\text{Degradation percentage (\%)} = (C_0 - C) / C_0 \times 100 \quad (2)$$

in which C_0 is the initial dye concentration and C being the dye concentration at time t , respectively. Photodegradation rate constant, k , was also calculated for all the samples.

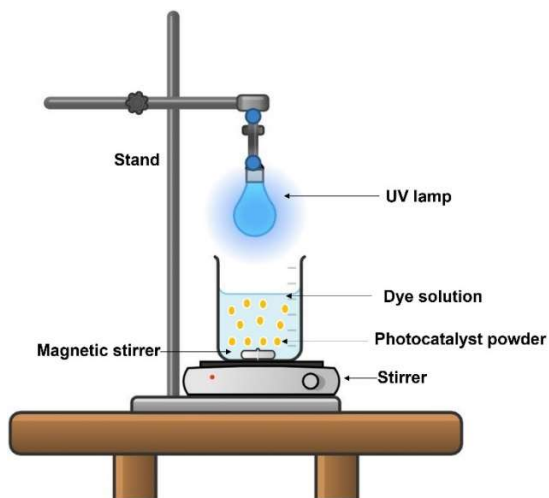


Figure 1. Schematic photodegradation measurement setup for degradation of methylene blue (MB)

Results and Discussion

Morphology of pure ZnO and Mg-doped ZnO

The morphology of pure ZnO and selected Mg-doped ZnO photocatalysts were recorded using FESEM and displayed in Figure 2. The images of pure ZnO (Figure 2(a) and (b)) were recorded at different magnification portrayed irregular rod-cubic like structures with approximately of 100- 500 nm dimensions. Image (c-d) and (e-f) represents 1 mol % Mg-doped ZnO and 10 mol % Mg-doped ZnO morphology and it was clearly seen that, similar rod-cubic like structures was formed for Mg-doped ZnO which were evenly distributed and well dispersed with the size similar to pure ZnO. Moreover, from the highly magnified image, the doping of Mg to the ZnO was not clearly shown. Besides, there are no significant changes on their size and morphology when Mg is doped to ZnO, and this might be due to the little amount of dopant that has been used during the synthesis method.

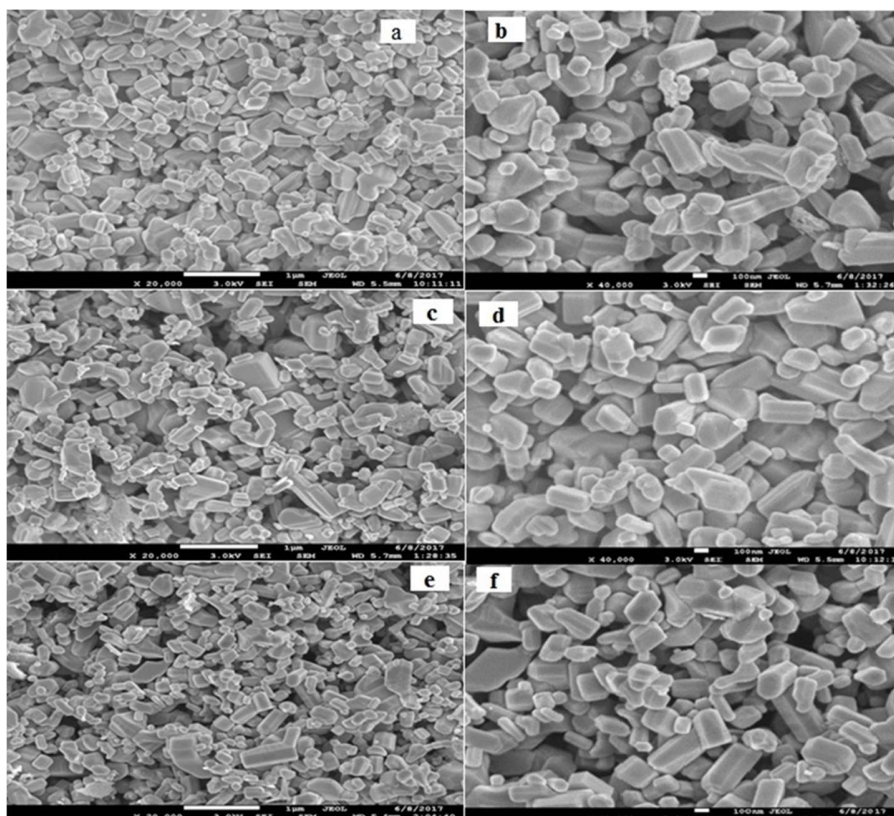


Figure 2. FESEM images of (a-b) pure ZnO, (c-d) 1 mol % Mg-doped ZnO and (d-e) 10 mol % Mg-doped ZnO at magnification 20, 000x and 40,000x

X-ray diffraction analysis

The structural properties of pure ZnO and Mg-doped ZnO photocatalysts were studied using XRD. Figure 3 represents the XRD spectra of pure ZnO and Mg-doped ZnO at different mol % of 1, 3, 5, 7 and 10, respectively. According to the XRD patterns, all the samples were highly crystalline with five major peaks that revealed the presence of hexagonal wurtzite structure of ZnO and the samples were excellent crystalline in nature. The diffraction peaks were identified at $2\theta = 31.75^\circ, 34.48^\circ, 36.20^\circ, 47.69^\circ, 56.72^\circ, 62.85^\circ, 66.53^\circ, 67.88^\circ$ and 69.09° indexed to (100), (002), (101), (102), (110), (103), (200), (112) and (201) being in good agreement with those of JCPDS card no. (No. 05-0664) [24, 27].

Besides, there were no corresponding peak related to Mg or MgO phase due to low amount of dopant that had been used during the synthesis method, which suggested that the presence of Mg was in the form of impurity atom [28, 29]. Similar phenomenon was also reported by Moulahi et al. [30] who prepared the Mg-doped ZnO nanostructures at different concentrations via a polyol process. They observed the pure phase formation of ZnO for all the composition of Mg-doped ZnO nanostructures. Furthermore, they also found a small shift towards a higher angle with Mg concentration, suggesting the decrease of the crystallites size and which similar findings had been observed in this work.

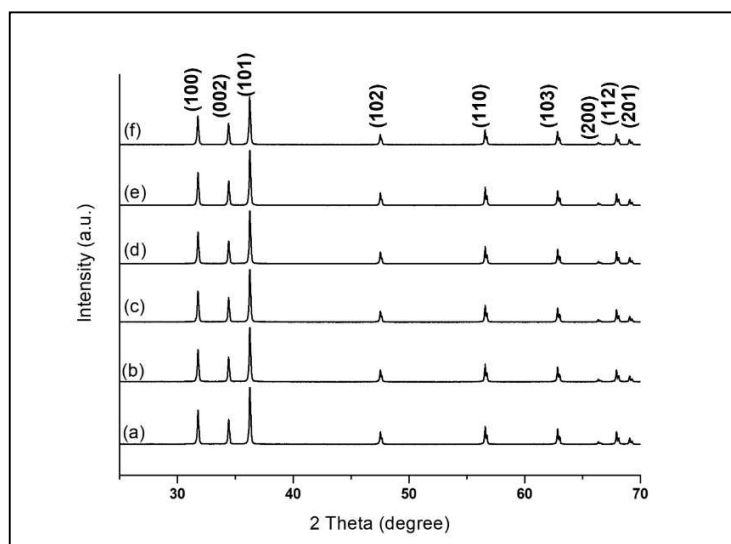


Figure 3. XRD spectra of (a) pure ZnO and Mg-doped ZnO at (b) 1, (c) 3, (d) 5, (e) 7 and (f) 10 mol % in the range of 25 – 70° prepared using modified sol-gel method

The estimated crystallite size was calculated using Scherrer equation and was found to be 81.64, 80.50, 80.12, 76.65, 76.17 and 74.82 nm for pure ZnO and Mg-doped ZnO with different concentration (1, 3, 5, 7 and 10 mol %) respectively. Table 1 shows the attributed peak, FWHM and calculated value of estimated crystallite size of pure ZnO and Mg-doped ZnO at different concentration. It can be observed that the FWHM value increased as higher concentration was incorporated into the ZnO from the pure ZnO up to 10 mol % Mg-doped ZnO and the estimated crystallite sizes

of the samples were found to decrease as the concentration of Mg dopant was increased. Based on Alam et al. [31] the diffraction peak shifted and wider FWHM with consistent increased in Mg doping is an indication of doping, suggesting a higher defect concentration and decreased quality of crystal with increased in Mg doping concentration. Moreover, because the ionic radii of Zn and Mg ions are similar (0.060 nm and 0.057 nm), Mg ions are expected to be replaced with Zn ions [32].

Table 1. Estimated crystallite size of pure ZnO and Mg-doped ZnO at different concentration obtained from (101) peak

Sample	Highest Peak (2 θ degrees)	FWHM, β (degrees)	Estimated Crystallite Size, D (nm)
Pure ZnO	36.25	0.10693	81.64
1 mol% Mg-doped ZnO	36.25	0.10845	80.50
3 mol% Mg-doped ZnO	36.25	0.10896	80.12
5 mol% Mg-doped ZnO	36.25	0.11390	76.65
7 mol% Mg-doped ZnO	36.25	0.11461	76.17
10 mol% Mg-doped ZnO	36.23	0.11668	74.82

Photocatalytic activities analysis

Photocatalytic degradation measurements were carried out for all photocatalyst. The degradation of MB dye was measured by using pure ZnO and Mg-doped ZnO photocatalyst at different concentrations i.e., 1, 3, 5, 7 and 10 mol%, respectively under UV light irradiation for 60 minutes. Figure 4(a) shows the percentage degradation of MB under the UV light tested with the pure ZnO and Mg-doped ZnO at different concentrations. From Figure 4(a), it can be observed that the percentage of degradation of 1 mol% shows the

highest percentage degradation with value of 89.54% compared to pure ZnO and other Mg-doped ZnO samples. Once 3 and 5 mol% was incorporated to the Mg-doped ZnO, the percentage of degradation showed a decrease pattern with the value of 82.99% and 84.78% and started to increase when doped with 7 (88.05%) and decreased back to 86.88% when 10 mol% Mg was applied indicating that optimization of concentration of dopant is significant to the performance of photocatalyst.

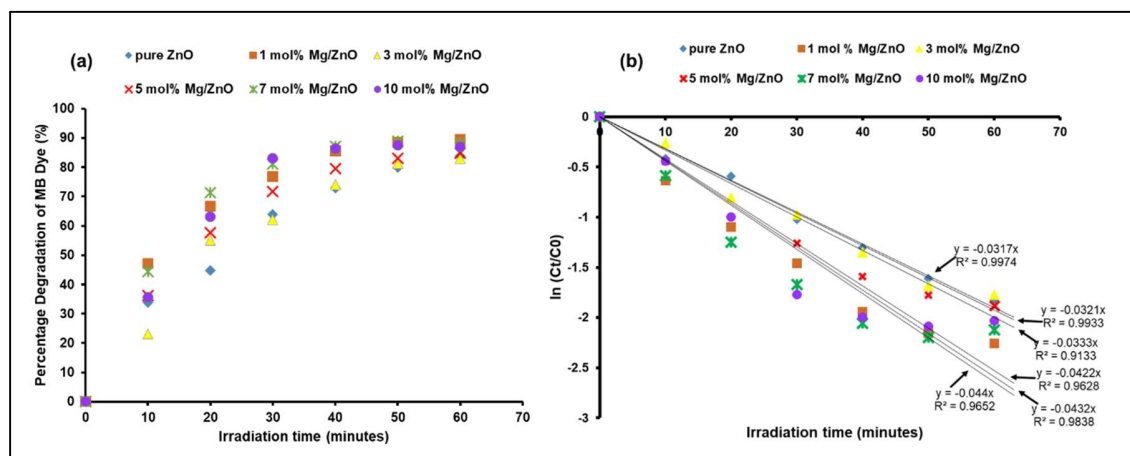


Figure 4. Plot of (a) Percentage of degradation of pure ZnO and Mg-doped ZnO and (b) $\ln(C/C_0)$ vs. irradiation time for the degradation of MB using pure ZnO and Mg-doped ZnO

Vargas et al. synthesized ZnO doped with MgO in different concentrations (1, 2 and 4 mol%) using Pechini polymer precursor method and reported on the effect of MgO doped on the pollutant removal [33]. They observed that the degradation of MO dye solution was effective using MgO doped ZnO compared to ZnO

samples and 2% Mg showed the most efficient in removing MO with a degradation percentage of 73% in 3 h irradiation time. Another study done by Okeke et al. worked on pure and Mg-doped ZnO prepared by one step simple process. They determined that the photodegradation performance of Mg-doped ZnO

against MB dye solution have a greater degradation percentage; more than 50% after 100 min of exposure light [32]. It is worth noting that the doped sample significantly enhanced the photocatalytic activities which is associated to the higher surface defects and smaller particle size, which consequently aid in the separation of photo-generated electron-holes pairs and slowing of their recombination rate.

The photodegradation rate constant, k of pure ZnO and Mg-doped ZnO has been assessed using the kinetic model suggested by Langmuir-Hinshelwood, which is pseudo-first kinetics model of photocatalysis [34] as stated in the Equation 3, as follows:

$$\ln(C_t/C_0) = -kt \quad (3)$$

Where C_t/C_0 is the ratio of dye concentration at adsorption-desorption equilibrium of those at different time intervals (t) and k is the photodegradation rate constant. The results are shown in Figure 4(b) and the photodegradation rate constant value, k was obtained from the linear fitting of the plotted graph. The observed k values are listed in Table 2 together with percentage

degradation of MB dye. It can be seen that, 1 mol% Mg-doped ZnO exhibited the highest photodegradation rate constant, k with value of 0.0432 min^{-1} compared to pure ZnO and other samples. Enhancement of the photocatalytic activity of 1 mol % Mg-doped ZnO compared to pure ZnO might be attributed to the increasing of surface area considering that the photocatalytic reaction occurred on the catalyst surface [35]. Moreover, as reported by Wang et al., doping of Mg^{2+} into ZnO increased the width of the band gap and therefore enhanced the photocatalytic performance as it could effectively delay the electron-hole recombination from valence band to conduction band [25]. Moreover, it can be observed that Mg-doped ZnO prepared by higher than 1 mol% Mg shows a decreasing performance which this might be due to an excessive Mg content which resulting in agglomeration of particles hence the photodegradation rate will be saturate. Samanta et al. reported that the photocatalytic performance was reduced when more Mg is loaded and concluded that there exists an optimum amount of Mg for enhancing the catalytic degradation process that influenced by band gap energy and crystallite size of the photocatalyst [36].

Table 2. Photocatalytic performance of pure ZnO and Mg-doped ZnO at different concentration

Sample	Percentage Degradation, (%) after 60 minutes	Photodegradation Rate Constant (k , min^{-1})	R ² Value
Pure ZnO	83.86	0.0317	0.9974
1 mol% Mg-doped ZnO	89.54	0.0432	0.9838
3 mol% Mg-doped ZnO	82.99	0.0321	0.9933
5 mol% Mg-doped ZnO	84.74	0.0333	0.9133
7 mol% Mg-doped ZnO	88.05	0.4290	0.9601
10 mol% Mg-doped ZnO	86.88	0.0422	0.9628

Conclusion

Mg-doped ZnO at various concentrations were successfully prepared using sol-gel method and characterized by FESEM and XRD analysis. XRD results revealed that Mg is substituted in ZnO without altering its hexagonal wurtzite structure. FESEM analysis revealed that surface features of ZnO shows an irregular rod-cubic like structures with approximately of 100- 500 nm dimensions for all samples. For

photodegradation analysis, after comparison with pure ZnO and other doped Mg-doped ZnO samples, 1 mol % Mg-doped ZnO exhibited better photocatalytic activity with degradation percentage of 89.54 % and photodegradation rate constant, k value of 0.0432 min^{-1} , respectively. These results suggest that doping play a crucial role in the efficiency of ZnO photocatalytic activities and the improved performance of Mg-doped ZnO suggests that it could be used as an alternate

photocatalyst for environmental problem.

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