Journal of Sustainability Science and Management *eISSN: 2672-7226*
Volume 14 Number 2, April 2019 : 1-10

PHOTOCATALYTIC DEGRADATION OF METHYLENE BLUE DYE USING CERIUM DOPED ZINC OXIDE NANOPARTICLES

NORADHIHA FARAHIN IBRAHIM[1], WAN RAFIZAH WAN ABDULLAH[1*], MAISHARA SYAZRINNI ROOSHDE[1], MOHD SABRI MOHD GHAZALI[2,3] AND WAN MOHD NORSANI WAN NIK[1]

[1]*School of Ocean Engineering, Universiti Malaysia Terengganu, 21030 Kuala Nerus, Terengganu, Malaysia*
[2]*School of Fundamental Science, Universiti Malaysia Terengganu, 21030 Kuala Nerus, Terengganu, Malaysia*
[3]*Institute of Tropical Biodiversity and Sustainable Development, Universiti Malaysia Terengganu, 21030 Kuala Nerus, Terengganu, Malaysia*

**Corresponding author: wanrafizah@umt.edu.my*

Abstract: Dyes released from textile and dyeing industries can distress the environment and becomes a threat to human health. In this study, the photocatalytic efficiency of cerium (Ce) doped ZnO photocatalyst to remove azo-dye is highlighted. Different concentrations of Ce (0.2, 0.4, 0.6, 0.8 and 1.0 mol %) were doped into ZnO and the as-prepared powder was characterized by using X-ray diffraction analysis (XRD), Fourier transforms infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM). Photodegradation of 10 mg/l of methylene blue (MB) dye solution has been conducted under UV-C (λ=254 nm) irradiation up to 180 minutes using 0.5 to 2.5 g/L of Ce doped ZnO powder. The findings revealed that photodegradation of MB increased with increasing Ce doping concentration and the addition of photocatalyst loads up to 2.0 g/L. Photocatalyst comprising 1 mol % Ce doped ZnO performed the highest photocatalytic activity with the efficiency of 94.24%.

KEYWORDS: Ce doped ZnO, photocatalyst, methylene blue, sustainable water treatment

Introduction

Dyes discharged from textile, food and dyeing industries generate water pollutants that can distress the environment and threaten human health. Conventional treatment methods including chemical precipitation, coagulation, ultrafiltration and biological methods have been used to remove these hazardous pollutants (Daneshvar *et al.,* 2004; Faisal *et al.,* 2011). However, most of these techniques are less sustainable as they fail to completely remove the toxic substances from the environment while some producing secondary wastes.

ZnO based photocatalysis system has a promising ability for enhancing the degradation of contaminants in wastewater (Chang *et al.,* 2014). The n-type ZnO offers many interesting features as photocatalyst including non-toxicity, excellent photo-reactivity and it has relatively lower synthesis cost compared to certain semiconductor photocatalysts (Kumar *et al.,* 2015; Moezzi *et al.,* 2012). The functionality of ZnO can be further modified through doping techniques. Sin *et al.,* (2014) suggested that doping lanthanide elements into host semiconductor will enable traps for photogenerated production of charge carriers and decrease the electron–hole pair recombination rate. As a result, the catalyst with enhanced photocatalytic performance and stability can be obtained.

In the present work, cerium (Ce) doped ZnO nanoparticles were synthesized through the combination of modified citrate gel and solid state route. Their photocatalytic properties as a function of Ce doping and catalyst loadings under UV light irradiation for photodegradation of MB dye as Model azo-dye are discussed.

Materials and Methods

Materials

Raw materials for synthesizing the photocatalyst powder were prepared according to nominal chemical composition of (100-x) mol% ZnO + x mol% CeO_2 where x = 0.2, 0.4, 0.6, 0.8 and 1.0. Commercial ZnO with the particle

size of less than 100 nm was used as the host material. Cerium (III) nitrate hexahydrate ($Ce(NO_3)_3.6H_2O$) with 99.99% purity was selected as the precursor for dopant and citric acid anhydrous ($C_6H_8O_7$) with 99.5% purity was used as the complexing agent. Methylene blue (MB) dye was used as Model azo-dye and its solution was prepared from methylene blue trihydrate ($C_{16}H_{24}ClN_3O_3S$).

Synthesis of Ce doped ZnO Photocatalyst Powder

Ce doped ZnO powder was synthesized through modified citrate gel and solid state routes. In the first stage, citric acid and Ce nitrate were mixed at a molar ratio of 3:1 in deionized water under constant stirring at 70-80˚C for 1 hour. ZnO powder was gradually mixed into the solution mixture of citric acid and Ce nitrate for 4 hours at 110˚C. Then as required, it was further dried in an oven for 19 hours at 120˚C before the mixture was pulverized and calcined for 4 hours at 500˚C at heating rate of 3˚C/min. Final sintering at 1200˚C for 5 hours at heating rate of 5˚C/min was performed to convert precursor completely into Ce doped ZnO powder.

Characterizations

Phase analysis performed by Miniflex II Benchtop X-ray Diffractometer (XRD) and FT-IR analysis was completed using Thermo Nicolet Avatar 380 FT-IR spectroscopy to confirm the chemical composition of the prepared powder. The microstructure was studied using scanning electron microscopy, SEM (JSM 6610LV-JEOL) and FESEM (FEI Nova™, NanoSEM 630 Series). Degradation of MB dye was monitored by using Perkin Elmer Lambda 25 Ultraviolet-visible (UV-Vis) spectrophotometer.

Evaluation of Photocatalytic Performance

Photocatalytic efficiency of Ce doped ZnO powder was evaluated from MB photodegradation testing. The photodegradation reaction was carried out in a 1 L beaker equipped with 11-watt UV-C lamp (λ=254 nm) containing 10 mg/L of MB dye solution. Photocatalyst added at different loads ranging between 0.5-2.5 g/L while continuous aeration of 12 L/min of air was applied. Before exposure to the UV light, a 30 minutes treatment in the dark was performed to achieve adsorption equilibrium of dye onto the photocatalyst surface. Every 15 minutes, 10 mL of the sample was withdrawn and for 10 minutes, centrifuged at 4000 rpm to separate the catalyst from the treated solution before further analysis. The degradation of MB dye was analysed using UV-Visible (UV-Vis) spectrophotometer. The presence of MB indicated by the emergence of absorbance peak at λ_{max} of 665 nm. The percentage of photocatalytic efficiency, *R* was calculated using the expression in Equation 1.

$$\text{Photocatalytic efficiency, R (\%)} = \frac{(C_o - C_t)}{C_o} \times 100 \qquad (1)$$

Where C_o is the initial concentration of dye (mg/L) (after 30 min treatment in dark) and C_t is the concentration of dye at irradiation time, t (mg/L).

Results and Discussion

Characteristics of Ce doped ZnO Powder

SEM images in Figure 1 shows the microstructure of pristine ZnO powder underwent sintering at 1200 °C for 5 hours whereas SEM images depicted in Figure 2 indicate microstructure of Ce doped ZnO sintered at similar condition.

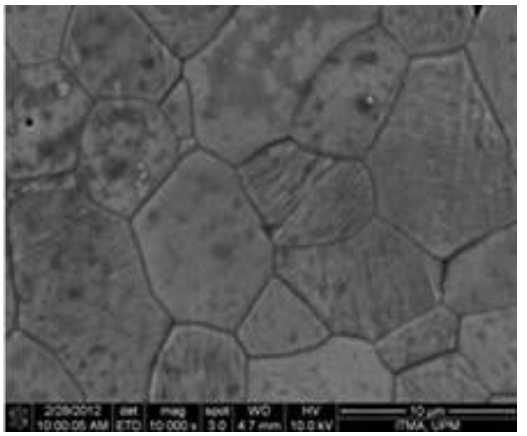

Figure 1: SEM image of pristine ZnO after sintering at 1200 °C.

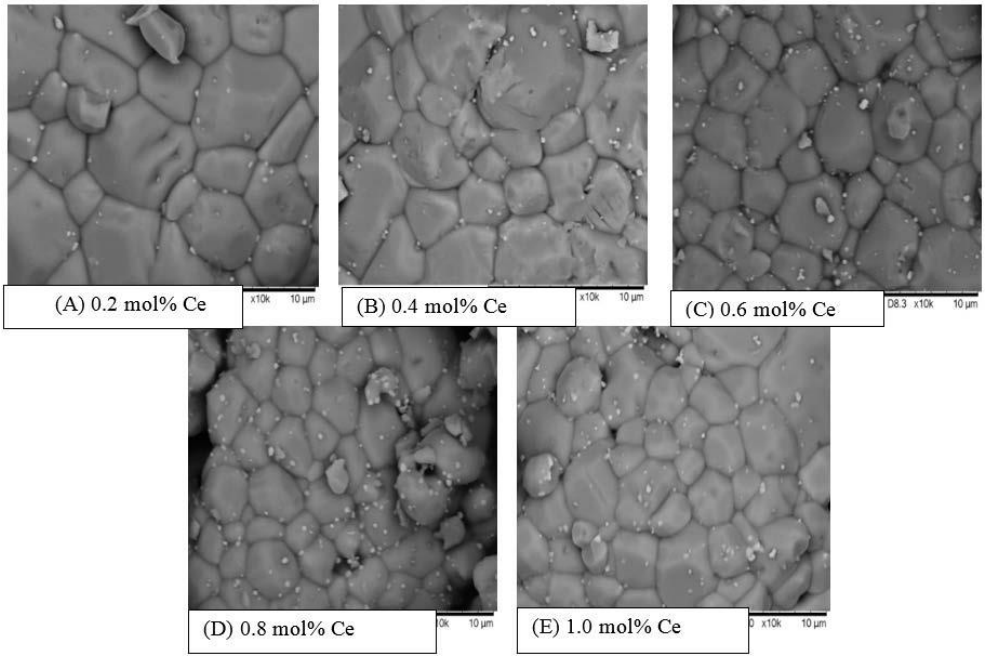

Figure 2: SEM image of pristine ZnO after sintering at 1200°C

In comparison, the grains of purely sintered ZnO powder were large (~5 – 18 µm) and less uniform. Ce doped ZnO, on the other hand, has relatively finer grained microstructure as compared to that of undoped ZnO. The general range of ZnO grains in doped ZnO was less than 8 µm. The high temperature sintering process caused the ZnO grains to coalesce with neighbouring grains. Nodules of CeO_2 precipitation was also detected forming on the surface of ZnO grains (visible as a bright spot on or in between ZnO grains). Higher Ce concentrations, particularly above 0.4 mol%, cause more obvious suppression effect on the ZnO grain growth, thus producing catalyst powder with finer grains (less than 5 µm). Similar morphology reported in Faisal *et al.*, (2011). Histograms presented in Figure 3 show the distributions of ZnO grain size for Ce doped ZnO containing different doping concentration of Ce. This is based on the measurement performed on 50 randomly selected grains on SEM images. The addition of higher mole of Ce into ZnO can be seen producing a powder with smaller grains and more consistent size. This evidenced is based on the formation of right skewed distribution as the frequency for smaller grains found in the sample increased.

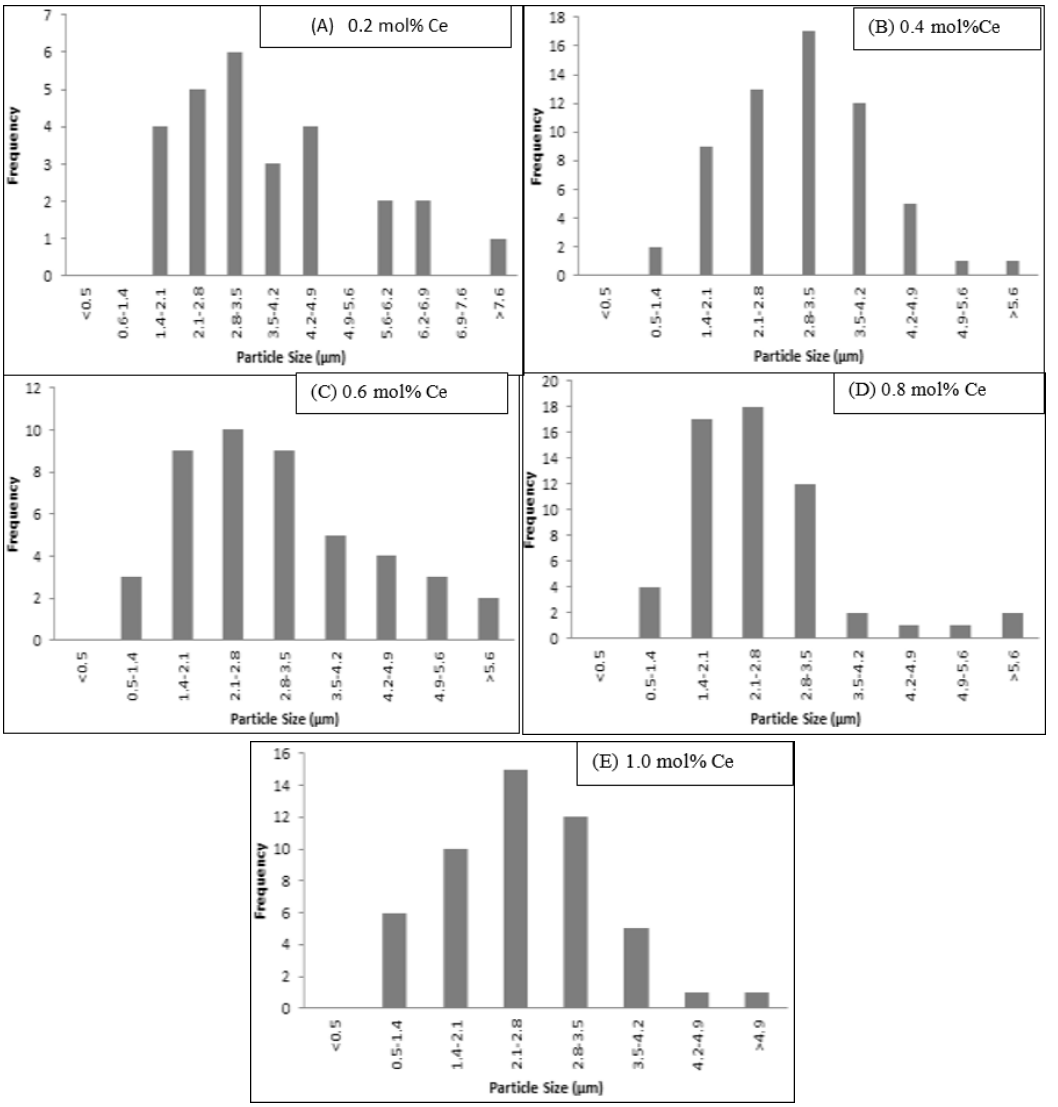

Figure 3: Distribution of ZnO grain in ZnO powder doped with (A) 0.2 mol%, (B) 0.4 mol%, (C) 0.6 mol%, (D) 0.8 mol% and (E) 1 mol% Ce.

Figure 4 shows the XRD patterns collected from Ce doped ZnO containing various amount of Ce. Strong diffraction peaks of ZnO are detected in the sample at 2θ of 31.8˚, 34.5˚, 36.3˚, 47.5˚, 56.6˚, 62.9˚, 66.4˚, 68.0˚, 69.1˚, 72.6˚ and 77.0˚, corresponding to the lattice planes of (100), (002), (101), (102), (110), (103), (200), (112), (201), (004) and (202). The results are in good agreement with the reference data for hexagonal wurtzite structured ZnO (PDF 79-2205) and the reported literature (Faisal *et al.*, 2013; Li *et al.*, 2012; Kumar *et al.*, 2015). Low intensity peaks belong to CeO_2 appears in the sample at 2θ of 28.6˚ and was assigned to (111) plane for the cubic fluorite CeO_2 (PDF 81-792) (Kannadasan *et al.*, 2014; Yousefi *et al.*, 2011). The XRD results confirmed the successful preparation of Ce doped ZnO from its precursor.

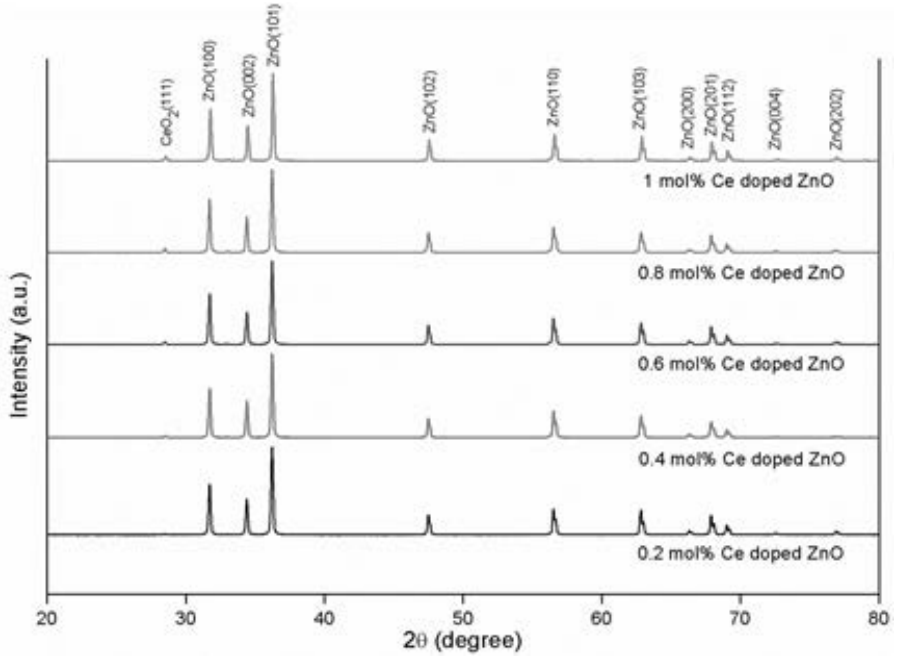

Figure 4: XRD patterns for 0.2 mol%, 0.4 mol%, 0.6 mol%, 0.8 mol% and 1 mol% Ce doped ZnO powder.

Figure 5 depicts the FT-IR spectra of Ce doped ZnO powder. The peak appears at wave number below 500 cm^{-1} attributed to the Ce-O bands (Gopinanthan *et al.*, 2015; Athawale *et al.*, 2009; Palard *et al.*, 2010). A band at 510 cm^{-1} is associated with metal-oxygen bonds (Zn-O) which confirms the presence of ZnO (Faisal *et al.*, 2013; Dar *et al.*, 2012).

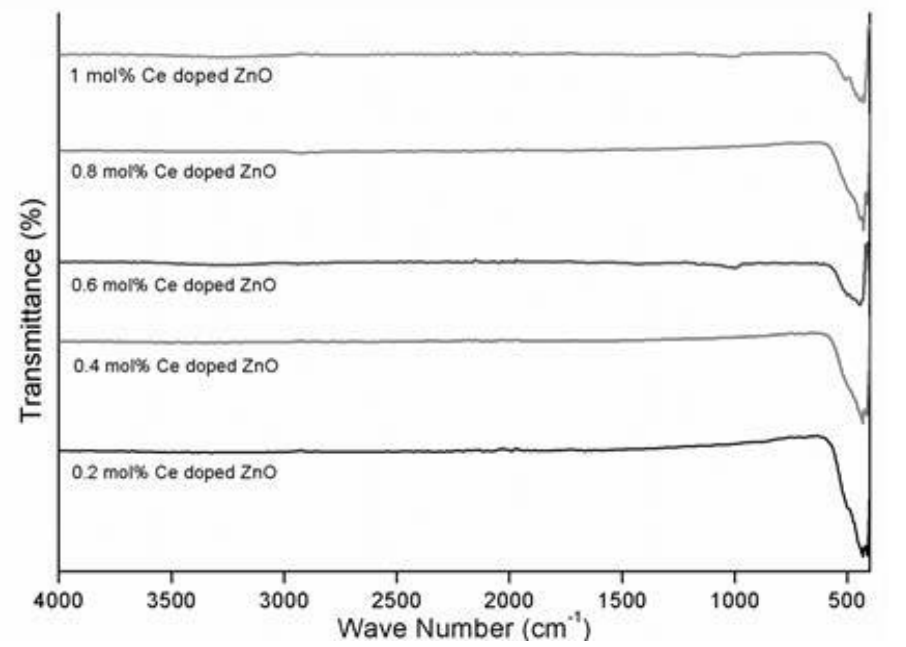

Figure 5: FT-IR spectra for 0.2 mol%, 0.4 mol%, 0.6 mol%, 0.8 mol% and 1 mol% Ce doped ZnO powder.

Photodegradation Performance of Ce doped ZnO

Based on the observation, synthesized powder exhibited photoreactivity in the presence of UV light. Figure 6 depicts the variation in UV-Vis spectra of MB dye treated under UV light in the presence of 2.0 g/L of ZnO doped with 1.0 mol% Ce. The strong absorption band at λ_{max}= 665 nm which corresponds to MB dye gradually decreased with increasing treatment time. This finding implies that the dye molecules underwent decomposition throughout the process and the presence of Ce doped ZnO effectively promoted the decomposition. Straumal *et al.,* (2011) stated, adsorption ability of catalyst surfaces and interfaces will be greatly enhanced by the presence of very fine-grained oxides. The smaller the grains, the higher the photoactivity of the catalyst.

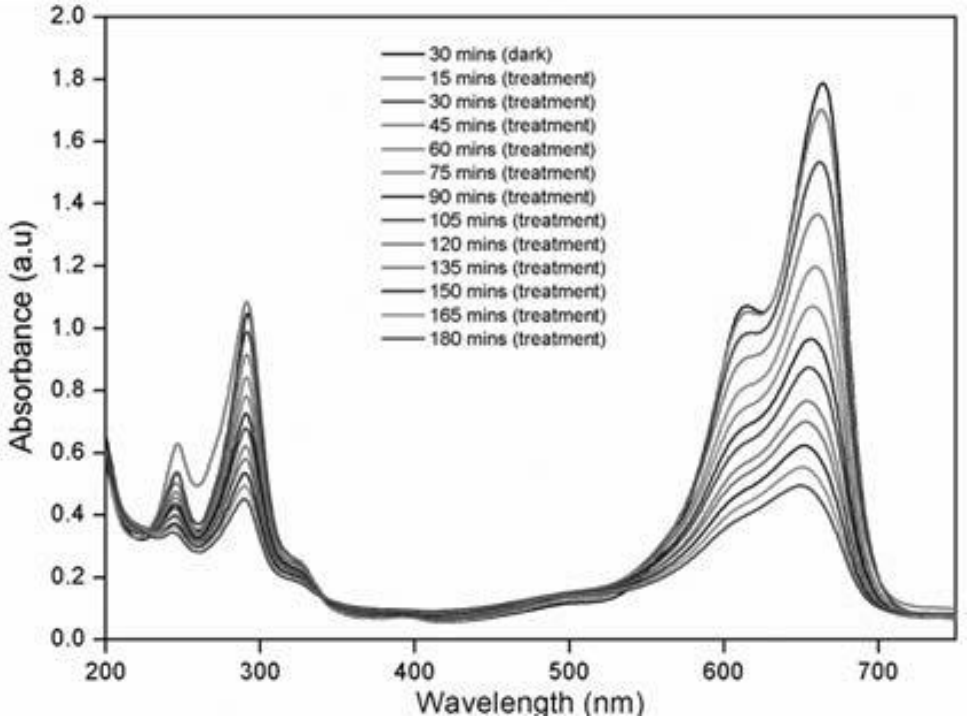

Figure 6: Variations in absorption spectra of MB dye in presence of 2.0 g/L 1.0 mol% Ce doped ZnO nanoparticles.

Effect of Ce Doping Concentration

Summarized in Table 1, Figure 7 demonstrates the effect of Ce doping concentration on the photocatalytic degradation of MB dye and the corresponding R value. The catalyst loading was fixed at 2.0 g/L whereas the Ce dopant concentration, varied between 0.2 to 1.0 mol%. An increase in Ce doping concentration up to 1 mol% showed the rise of percentage photocatalytic effieiency, R. On the basis of electrons and holes migration, this can be elucidated on the photocatalyst surface and the penetration of UV irradiation into the solution (Kumar *et al.,* 2015). By doping ZnO with Ce^{4+}, trapping sites of charge carriers increases with the elevated amount of dopant concentration which lengthen the lifetime of carriers (Rezaei & Habibi, 2013). On the basis of microstructure, photocatalyst with the higher Ce doping has finer grain microstructure. Thus, it has a larger catalytic surface and better contact with MB molecules. The Ce doping concentration with the highest photocatalytic reactivity was determined at 1 mol% with the value of R of 94.24%.

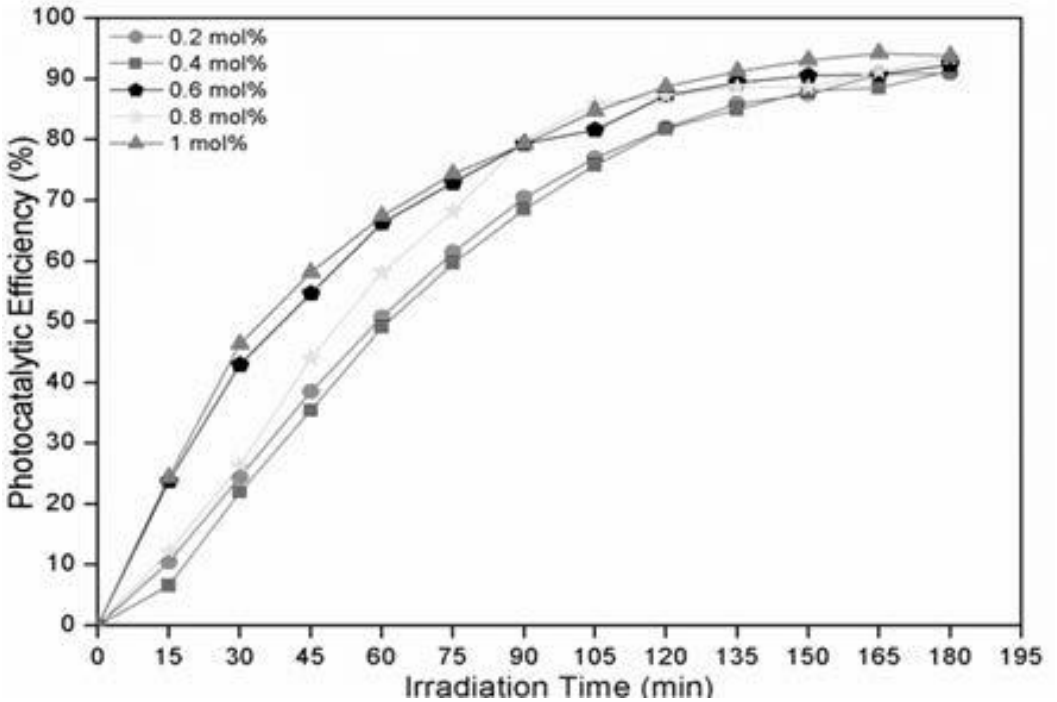

Figure 7: Percentage photocatalytic efficiency of MB dye with vary concentration (0.2 mol%, 0.4 mol%, 0.6 mol%, 0.8 mol% and 1 mol%) Ce doped ZnO nanoparticles.

Table 1: Photocatalytic efficiency value with Ce doping concentration

Ce doping concentration (mol %)	Photocatalytic efficiency, R (%)
0.2	90.94
0.4	91.33
0.6	92.32
0.8	93.51
1.0	94.24

Effect of Photocatalyst Loading

Optimum photocatalyst loading should be determined for a cost-efficient photodegradation process. Figure 8 shows the variation in photocatalytic efficiency, R for 1 mol% Ce doped ZnO with increasing loading (0.5 to g/L). An increase in catalyst loading led to improvement in R values. Within 180 minutes, the value of R increased from 77.20 to 94.24%. The enhancement of photocatalytic activity is associated with the increment in the number of active sites as a result of higher catalyst dosage per unit volume. This activity increased the number of hydroxyl and superoxide radicals (Subash *et al.*, 2012; Chakrabarti & Dutta, 2004; Pare *et al.*, 2008). The catalyst loading resulted in the highest R was determined at 2.0 g/L. Conversely, increasing the catalyst loading beyond 2.0 g/L caused the R value to gradually decrease. As the turbidity of the suspension elevated, the light scattering and screening effect took place causing some of the photocatalyst particles could not be activated (Gnanaprakasam *et al.*, 2015).

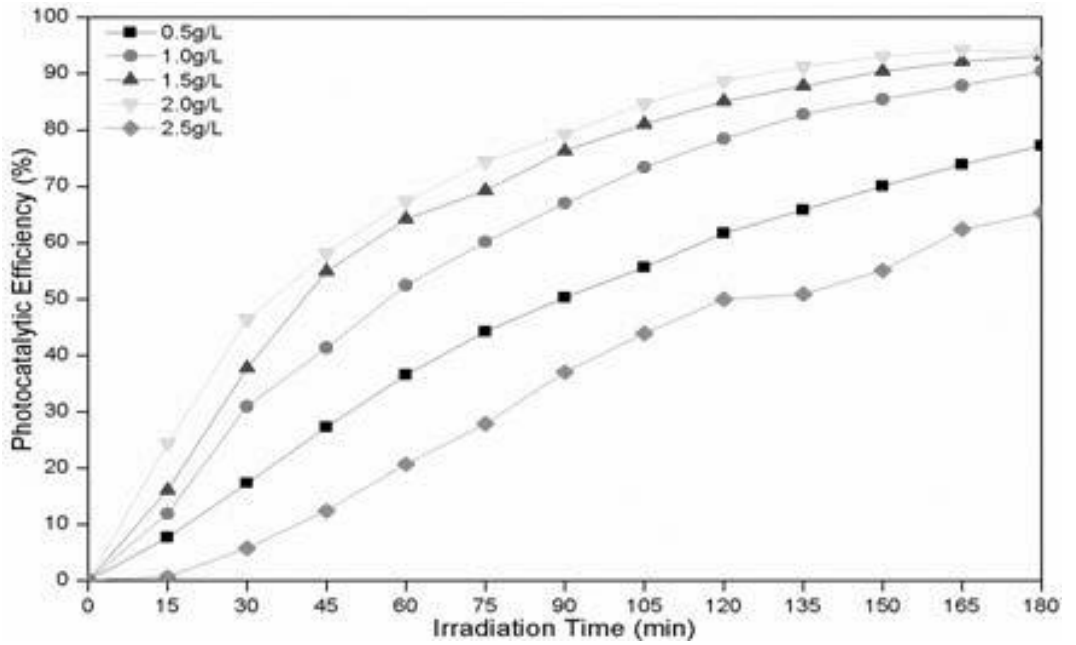

Figure 8: Percentage photocatalytic efficiency of MB dye with varied catalyst loadings (0.5, 1.0, 1.5, 2.0 and 2.5 g/L).

Conclusions

Ce doped ZnO photocatalyst powder was successfully synthesized through a combination of modified citrate gel method and solid state routes. XRD, SEM and FT-IR analyses confirmed the synthesized powder contained finely grained (less than 8 µm) hexagonal wurtzite structured ZnO along with dopant, CeO_2 with cubic fluorite structure. The photocatalytic efficiency of Ce doped ZnO to assist the degradation of MB dye increased with Ce doping and the amount of catalyst used. The maximum photocatalytic efficiency was achieved at the highest doping concentration of 1 mol% Ce and the catalyst loading of 2.0 g/L. According to these findings, Ce doped ZnO is indeed a promising photocatalyst with tailorable properties for inducing decomposition of organic dyes or other similar aqueous contaminants.

Acknowledgments

The authors would like to acknowledge the financial support from research grant provided by Ministry of Higher Education under Fundamental Research Grant Scheme (FRGS), Grant No: 59436 and Universiti Malaysia Terengganu for providing the facilities and funding through TPM 68006/2016/75.

References

Athawale, A. A., Bapat, M. S., & Desai, P. A. (2009). Hydroxide directed routes to synthesize nanosized cubic ceria (CeO_2). *Journal of Alloys and Compounds*, 484(1-2), 211-217.

Chakrabarti, S., & Dutta, B. K. (2004). Photocatalytic degradation of model textile dyes in wastewater using ZnO as semiconductor catalyst. *Journal of Hazardous Materials*, *112*(3), 269-278.

Chang, C. J., Lin, C. Y., & Hsu, M. H. (2014). Enhanced photocatalytic activity of Ce-doped ZnO nanorods under UV and visible light. *Journal of the Taiwan Institute of Chemical Engineers*, *45*(4), 1954-1963.

Daneshvar, N., Salari, D., & Khataee, A. R. (2004). Photocatalytic degradation of azo dye acid red 14 in water on ZnO as an alternative catalyst to TiO_2. *Journal of Photochemistry and Photobiology A: Chemistry, 162*(2-3), 317-322.

Dar, G. N., Umar, A., Zaidi, S. A., Ibrahim, A. A., Abaker, M., Baskoutas, S., & Al-Assiri, M. S. (2012). Ce-doped ZnO nanorods for the detection of hazardous chemical. *Sensors and Actuators B: Chemical, 173*, 72-78.

Faisal, M., Khan, S. B., Rahman, M. M., Jamal, A., Akhtar, K., & Abdullah, M. M. (2011). Role of ZnO-CeO_2 nanostructures as a photo-catalyst and chemi-sensor. *Journal of Materials Science & Technology, 27*(7), 594-600.

Faisal, M., Ismail, A. A., Ibrahim, A. A., Bouzid, H., & Al-Sayari, S. A. (2013). Highly efficient photocatalyst based on Ce doped ZnO nanorods: Controllable synthesis and enhanced photocatalytic activity. *Chemical Engineering Journal, 229*, 225-233.

Gnanaprakasam, A., Sivakumar, V. M., & Thirumarimurugan, M. (2015). Influencing parameters in the photocatalytic degradation of organic effluent via nanometal oxide catalyst: A review. *Indian Journal of Materials Science, 2015*, 1-16.

Gopinathan, E., Viruthagiri, G., & Shanmugam, N. (2015). Optical, surface analysis and antibacterial activity of ZnO–CuO doped cerium oxide nanoparticles. *Optik-International Journal for Light and Electron Optics, 126*(24), 5830-5835.

Kannadasan, N., Shanmugam, N., Cholan, S., Sathishkumar, K., Viruthagiri, G., & Poonguzhali, R. (2014). The effect of Ce^{4+} incorporation on structural, morphological and photocatalytic characters of ZnO nanoparticles. *Materials Characterization, 97*, 37-46.

Kumar, R., Umar, A., Kumar, G., Akhtar, M. S., Wang, Y., & Kim, S. H. (2015). Ce-doped ZnO nanoparticles for efficient photocatalytic degradation of direct red-23 dye. *Ceramics International, 41*(6), 7773-7782.

Li, C., Zhang, X., Dong, W., & Liu, Y. (2012). High photocatalytic activity material based on high-porosity ZnO/CeO_2 nanofibers. Materials Letters, 80, 145-147.

Moezzi, A., McDonagh, A. M., & Cortie, M. B. (2012). Zinc oxide particles: Synthesis, properties and applications. Chemical Engineering Journal, 185, 1-22.

Palard, M., Balencie, J., Maguer, A., & Hochepied, J. F. (2010). Effect of hydrothermal ripening on the photoluminescence properties of pure and doped cerium oxide nanoparticles. *Materials Chemistry and Physics, 120*(1), 79-88.

Pare, B., Jonnalagadda, S. B., Tomar, H., Singh, P., & Bhagwat, V. W. (2008). ZnO assisted photocatalytic degradation of acridine orange in aqueous solution using visible irradiation. *Desalination, 232*(1-3), 80-90.

Rezaei, M., & Habibi-Yangjeh, A. (2013). Simple and large scale refluxing method for preparation of Ce-doped ZnO nanostructures as highly efficient photocatalyst. *Applied Surface Science, 265*, 591-596.

Sin, J. C., Lam, S. M., Lee, K. T., & Mohamed, A. R. (2014). Preparation of rare earth-doped ZnO hierarchical micro/nanospheres and their enhanced photocatalytic activity under visible light irradiation. *Ceramics International, 40*(4), 5431-5440.

Straumal, B., Mazilkin, A., Protasova, S., Myatiev, A., Straumal, P., Goering, E., & Baretzky, B. (2011). Influence of texture on the ferromagnetic properties of nanograined ZnO films. *Physica Status Solidi (b), 248*(7), 1581-1586.

Subash, B., Krishnakumar, B., Velmurugan, R., Swaminathan, M., & Shanthi, M. (2012). Synthesis of Ce co-doped Ag–ZnO photocatalyst with excellent performance

for NBB dye degradation under natural sunlight illumination. *Catalysis Science & Technology, 2*(11), 2319-2326.

Yousefi, M., Amiri, M., Azimirad, R., & Moshfegh, A. Z. (2011). Enhanced photoelectrochemical activity of Ce doped ZnO nanocomposite thin films under visible light. *Journal of Electroanalytical Chemistry, 661*(1), 106-112.