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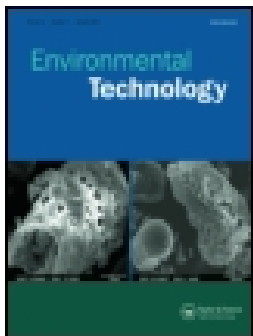
Syaiful Akhmal Saadon, *University Technology Malaysia*

Palanivel Sathishkumar, *University Technology Malaysia*

Abdull Rahim Mohd Yusoff, *University Technology Malaysia*

Mohd Dzul Hakim Wirzal, *University Technology Malaysia*

Muhammad Taufiq Rahmalan, *University Technology Malaysia*, et al.



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## Photocatalytic activity and reusability of ZnO layer synthesised by electrolysis, hydrogen peroxide and heat treatment

Syaiful Akhmal Saadon<sup>a</sup>, Palanivel Sathishkumar<sup>b</sup>, Abdull Rahim Mohd Yusoff<sup>b,c</sup>, Mohd Dzul Hakim Wirzal<sup>c</sup>, Muhammad Taufiq Rahmalan<sup>c</sup> and Hadi Nur<sup>d</sup>

<sup>a</sup>Department of Environmental Engineering, Faculty of Civil Engineering, Universiti Teknologi Malaysia, Skudai, Malaysia; <sup>b</sup>Centre for Environmental Sustainability and Water Security (IPASA), Research Institute for Sustainable Environment (RISE), Universiti Teknologi Malaysia, Skudai, Malaysia; <sup>c</sup>Department of Chemistry, Universiti Teknologi Malaysia, Skudai, Malaysia; <sup>d</sup>Ibnu Sina Institute for Fundamental Science Studies, Universiti Teknologi Malaysia, Skudai, Malaysia

### ABSTRACT

In this study, the zinc oxide (ZnO) layer was synthesised on the surface of Zn plates by three different techniques, i.e. electrolysis, hydrogen peroxide and heat treatment. The synthesised ZnO layers were characterised using scanning electron microscopy, X-ray diffraction, UV-visible diffuse reflectance and photoluminescence spectroscopy. The photocatalytic activity of the ZnO layer was further assessed against methylene blue (MB) degradation under UV irradiation. The photocatalytic degradation of MB was achieved up to 84%, 79% and 65% within 1 h for ZnO layers synthesised by electrolysis, heat and hydrogen peroxide treatment, respectively. The reusability results show that electrolysis and heat-treated ZnO layers have considerable photocatalytic stability. Furthermore, the results confirmed that the photocatalytic efficiency of ZnO was directly associated with the thickness and enlarged surface area of the layer. Finally, this study proved that the ZnO layers synthesised by electrolysis and heat treatment had shown better operational stability and reusability.

### ARTICLE HISTORY

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Advanced oxidation processes; electrolysis; heat treatment; hydrogen peroxide treatment; photocatalysis; zinc oxide

## 1. Introduction

Advanced oxidation processes (AOPs) are oxidative methods, which generate powerful oxidising agent hydroxyl radicals to destroy the pollutant in wastewater. [1] AOPs such as Fenton and photo-Fenton catalytic reactions,  $H_2O_2$ /UV processes and semiconductor photocatalysis have been studied under a broad range of experimental conditions in order to reduce the colour and organic load of the dying wastewater. [2] Currently, AOPs are being considered as the potential treatment process for effective and rapid degradation of pollutants.

Among the AOPs, semiconductor photocatalysis has attracted considerable attention in the last decades owing to complete elimination of environmental pollutant into carbon dioxide, water and mineral acids under UV light irradiation. [3] Over the last few years, a number of semiconductor photocatalysis have been studied for the organic pollutant degradation. [4] The most extensively studied photocatalysts are titanium dioxide ( $TiO_2$ ) and zinc oxide (ZnO). Interestingly, ZnO is an inexpensive, easily available semiconductor material, which shows higher decomposition rate against organic pollutant than  $TiO_2$ . [5] Therefore, the

ZnO-mediated photocatalytic process has received great interest for the degradation of organic pollutants.

Many synthetic dyes and their degradation products tend to have carcinogenic and toxic effects on the biotic communities, and pose severe environmental problems. [6] Therefore, the proper treatment of dye-contaminated wastewater is essential to prevent the ecological issues. Methylene blue (MB) is a model dye used extensively as an indicator for the photocatalytic activities owing to its absorption peaks in the visible range. Thus, its degradation can be easily monitored using UV-vis absorption spectroscopy. The peak height gradually decreases as the irradiation time increases; indicating the potential degradation of MB by the photocatalytic activity of catalysts. [7] ZnO is a polar molecule and has alternating planes consisting of  $O^{2-}$  and  $Zn^{2+}$  ions positioned along the *c* axis. Thus, the  $OH^-$  radicals could be adsorbed on the  $Zn^{2+}$  surfaces and also the cationic dye; MB can be adsorbed through  $OH^-$  radicals on the surface of photocatalyst ZnO, which is necessary for the MB degradation. [8]

A number of methods have been used to synthesise ZnO, including the hydrothermal process, vapour phase

growth, chemical solution route, thermal evaporation, UV light irradiation and sol–gel process.[9,10] Nevertheless, the available literatures clearly show that the thickness and surface area play an important role in the photocatalytic activities of semiconductors. Therefore, in this study to find out the effective photocatalytic activity, the ZnO layer was synthesised on the surface of Zn plates by three different techniques, i.e. electrolysis, hydrogen peroxide and heat treatment. Further, ZnO catalysts were characterised using scanning electron microscopy (SEM), X-ray diffraction (XRD), UV–visible diffuse reflectance (UV–Vis DR) and photoluminescence spectroscopy (PLS). Finally, in order to know the photocatalytic efficiency and reusability of the ZnO layer synthesised by three different methods, MB is used as a model dye for the degradation experiment.

## 2. Materials and methods

### 2.1. Chemicals

Zinc pure plates (BDH chemicals, 0.38 mm), Zn alloy plates (ZAMAK2), sodium hydroxide (Qrec), hydrochloric acid (Merck, 98%), hydrogen peroxide (Qrec, 30%), MB (Sigma–Aldrich) were used in this study.

### 2.2. Synthesis of ZnO catalyst

Zn plates were blasted with a sand blasting machine (Joylife JL-1212) to remove the naturally formed oxide layers on its surface and were cut to the size of 50 mm × 60 mm. Further, the ZnO layer on the Zn plates was synthesised by electrolysis, hydrogen peroxide and heat treatment.

#### 2.2.1. Electrolysis

In this method, Zn plates were set as anode and graphite plates were used as cathode. Electrolysis was conducted using 0.1 M of NaOH as the electrolyte solution. The distance between anode and cathode was fixed at 50 mm in electrolyte solution. The electrolyte was circulated using a magnetic stirrer at  $30 \pm 5^\circ\text{C}$ . A DC voltage (10 V) was applied to the cell for 1 h using a regulated DC power supply (PL 303). Then, the modified zinc plates were rinsed with deionised water and dried in a flow of cool air.

#### 2.2.2. Hydrogen peroxide treatment

For hydrogen peroxide-mediated ZnO layer preparation, Zn plates were dipped in 150 mL of  $\text{H}_2\text{O}_2$  (30%) solution and stirred on a magnetic stirrer at room temperature for 1 h. Then the treated Zn plates were thoroughly washed with deionised water and dried in a vacuum oven.

#### 2.2.3. Heat treatment

To prepare the ZnO layer by heat treatment, Zn plates were heated in a hot air oven at  $400^\circ\text{C}$  for 1 h. Then, the treated Zn plates were evaluated for photocatalytic performance to degrade the target pollutant.

### 2.3. Structural characterisation of ZnO catalysts

The synthesised ZnO catalysts were characterised using SEM (Philip XL40), XRD (Bruker AXS D8 advance), UV–Vis DR (Perkin Elmer, Lambda 900) and PLS (HMTECH, MFS-630 Multi) to determine their properties such as surface morphology, band-gap energy, adsorption edge, crystallinity and emission intensity.

### 2.4. Photocatalytic degradation of MB

The photocatalytic degradation of MB in aqueous solution was performed using synthesised ZnO catalysts. In the degradation reaction, 10 mg of the catalyst was added to 150 mL of MB solution (50 ppm) at pH 6.5. The reaction mixture was transferred to the photo-reactor and air was continuously supplied. At the beginning, the reaction mixture was not exposed to UV irradiation so as to ensure the adsorption process. After that the degradation reaction was performed under UV light irradiation (365 nm, 100 W) with constant stirring at  $30^\circ\text{C}$  for 5 h. During the reaction, 3 mL of samples was taken at regular intervals, and the centrifuged supernatant was used to monitor the degradation of MB in a UV–Vis spectrophotometer (Perkin Elmer Lambda 25) at 620 nm. The percentage of MB degradation was calculated by the following equation:

$$D = \frac{(A_i - A_f)}{A_i} \times 100, \quad (1)$$

where  $D$  is the percentage of MB degradation,  $A_i$  is the initial absorbance at a particular wavelength or the total area under plot and  $A_f$  is the final absorbance at a particular wavelength or the total area under plot. All of the experiments were performed in duplicates and the values of the average of two experiments are reported.

### 2.5. Reusability and photocatalytic stability of the synthesised ZnO catalyst

The reusability efficiency and photocatalytic stability of the synthesised ZnO catalysts were assessed against MB degradation over several cycles in batch mode. The MB degradation was performed as described in Section 2.4 of this paper. After the reaction, the ZnO catalyst from each cycle was thoroughly rinsed with deionised

water and then reintroduced into a fresh cycle. The MB degradation efficiency and photocatalytic stability of the ZnO layer were measured at the end of each cycle. The photocatalytic stability of the ZnO layer was calculated by the following equation:

$$PCA = \frac{C_n}{C_1} \times 100, \quad (2)$$

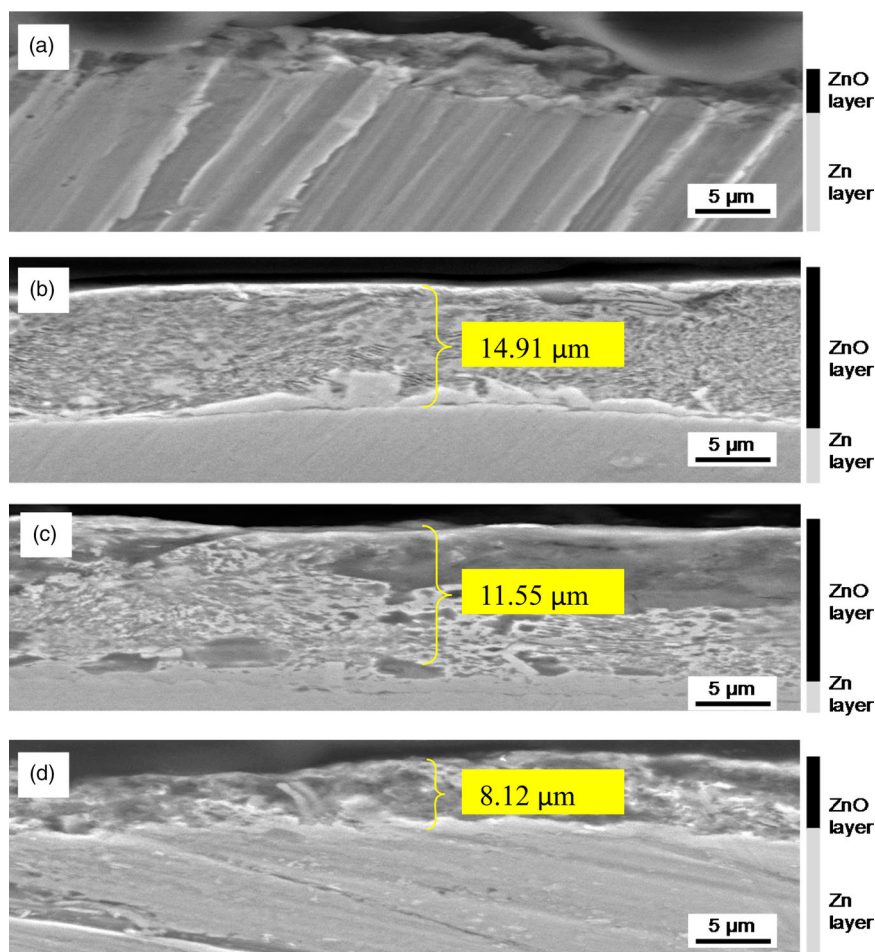
where PCA is the percentage of ZnO photocatalytic activity,  $C_n$  is the reaction time required for the maximum percentage (as achieved maximum percentage of degradation at a particular time point in the first cycle) of MB degradation at end of the particular cycle, and  $C_1$  is the maximum percentage of MB degradation achieved at a particular time point in the first cycle. All the experiments were performed at least twice using two replicates. The data presented in the figures correspond to the mean values with a standard error.

### 3. Results and discussion

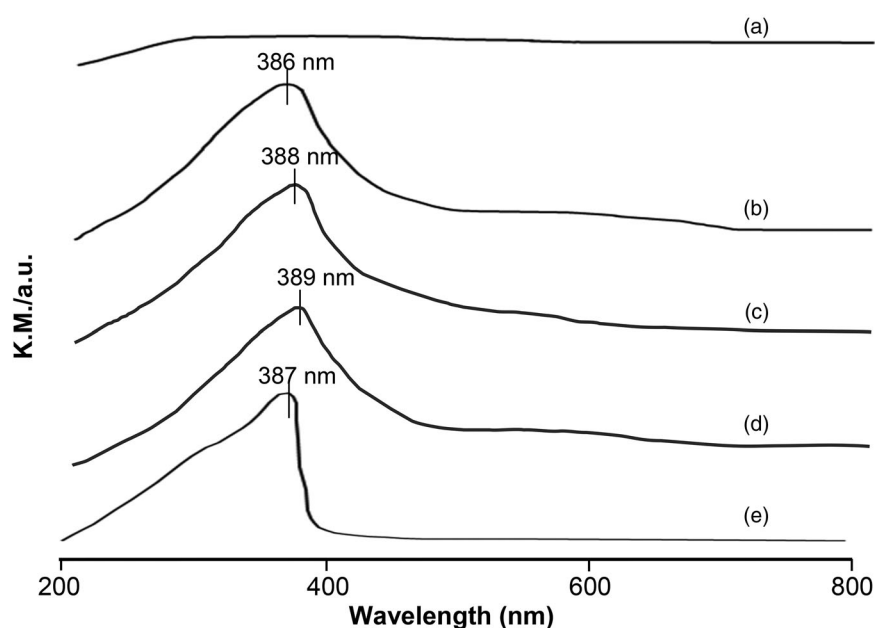
#### 3.1. Structural characterisation of ZnO catalysts

SEM was used to investigate the surface morphology of the synthesised ZnO layer on the Zn plates as shown in Figure 1. The thickness of the ZnO layer naturally formed on the surface of Zn plates was about 2.82  $\mu\text{m}$ . The SEM image shows that all the treated samples consist of the ZnO layer; however, the thickness of the layer considerably differed for each of the samples. The average thickness of the ZnO layer synthesised through electrolysis, heat and hydrogen peroxide treatment was found to be 14.91, 11.55 and 8.12  $\mu\text{m}$ , respectively. These results confirmed that the electrolysis is the best method to synthesise a thick layer of ZnO on the surface of Zn plates.

The band-gap energy of the synthesised catalysts is illustrated in Figure 2. The UV-Vis DR spectrum of commercial ZnO powder which shows a sharp adsorption of photon energy in the wavelength range of 387–350 nm was used as a reference to confirm the synthesised ZnO layer. The spectra showed that all three methods



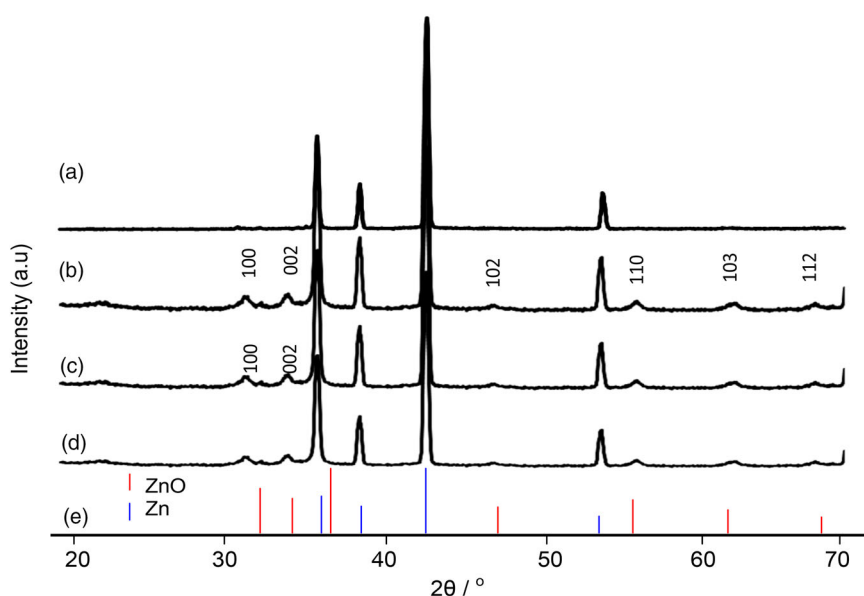
**Figure 1.** SEM image of (a) Zn plate, (b) Zn plate/electrolysis, (c) Zn plate/heat and (d) Zn plate/hydrogen peroxide.



**Figure 2.** UV-Vis DR spectrum of (a) Zn plate, (b) Zn plate/electrolysis, (c) Zn plate/heat, (d) Zn plate/hydrogen peroxide and (e) ZnO powder.

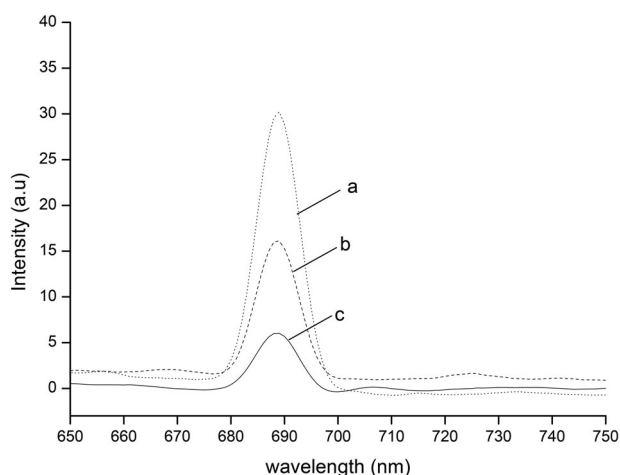
used in this study were able to synthesise the ZnO layer on the surface of Zn plates. It was calculated that the band-gap energies were 3.22, 3.20 and 3.19 eV for the ZnO layer as synthesised by the electrolysis, hydrogen peroxide and heat treatment techniques, where their adsorption edges occurred at wavelengths of 386, 388 and 389 nm, respectively. The absence of adsorption edge for the Zn plates was probably due to some defects such as oxygen vacancy, zinc vacancy, interstitial oxygen, interstitial zinc and anti-site oxygen existed in the naturally formed ZnO layer.[11]

Figure 3 shows the XRD results of the ZnO layer synthesised on Zn plates by different treatment techniques. The diffraction pattern of Zn metallic peaks for the synthesised ZnO layer on the surface of Zn plates found at  $2\theta$  of  $36.2^\circ$ ,  $38.9^\circ$ ,  $43.2^\circ$  and  $54.3^\circ$  is similar to the unmodified Zn plate. The XRD pattern of the ZnO layer synthesised on Zn plates by electrolysis, hydrogen peroxide and heat treatment shows the reflections (100) and (002) at  $2\theta$  of  $32.7^\circ$  and  $34.4^\circ$ , respectively. In the XRD pattern of the ZnO layer synthesised on Zn plates by these techniques, the reflections (100), (002),



**Figure 3.** X-ray diffractogram of (a) Zn plate, (b) Zn plate/electrolysis, (c) Zn plate/heat, (d) Zn plate/hydrogen peroxide and (e) JCPDS No. of 75-0576 and 04-0831.





**Figure 4.** PL spectrum of (a) Zn plate/hydrogen peroxide, (b) Zn plate/heat and (c) Zn plate/electrolysis.

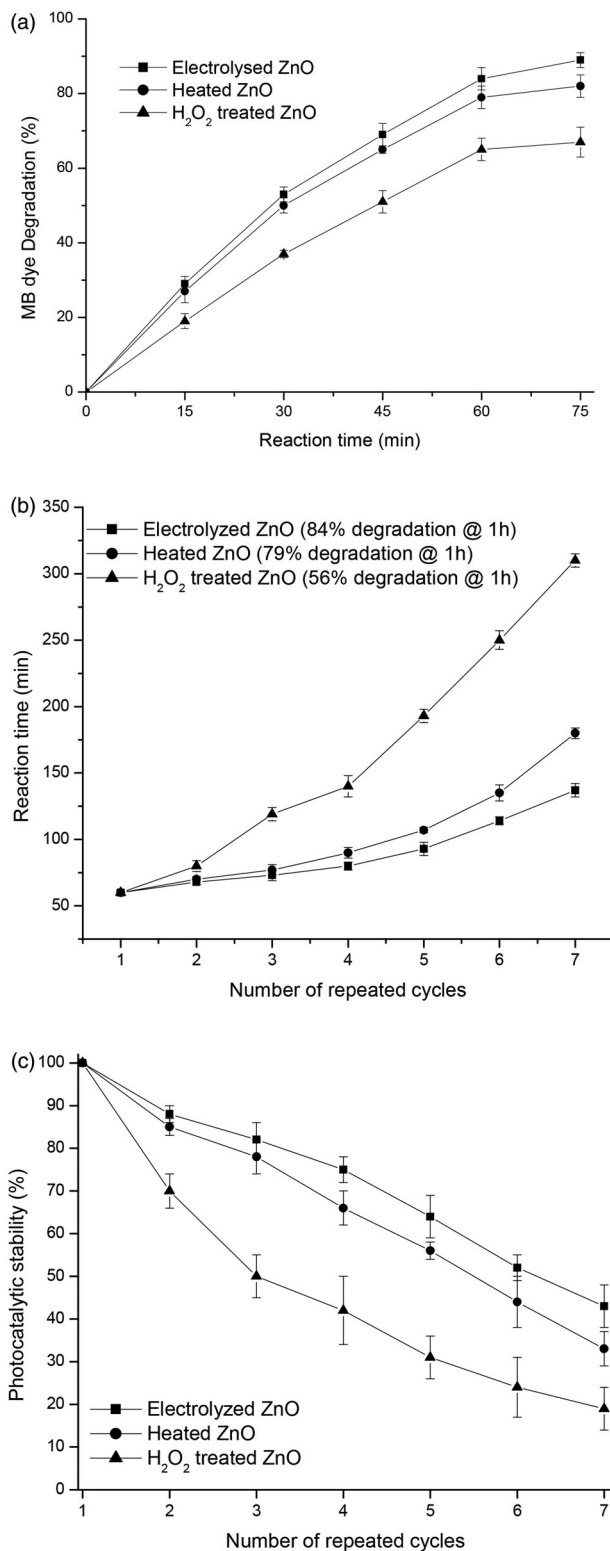
(102), (110), (103) and (112) were found to be appearing at  $2\theta$  of  $32.7^\circ$ ,  $34.4^\circ$ ,  $47.6^\circ$ ,  $56.7^\circ$ ,  $62.9^\circ$  and  $68.1^\circ$ , respectively. The ZnO layer synthesised in this study gives an XRD pattern quite similar to the XRD pattern of ZnO synthesised by thermal oxidation.[12] Therefore, it confirms that the modification of Zn plates by electrolysis, hydrogen peroxide and heat treatment techniques has a great tendency to form the ZnO layer with a crystalline structure. The crystallization of the ZnO layer synthesised by all methods used in this study was found to be moderate.

The analysis of PLS emission peaks is an appropriate technique in determining the effectiveness of charge carrier trapping, migration and transfer, and most helpful in order to understand the fate of electron-hole pairs in semiconductor particles, since it results from the recombination of excited electrons and holes. A lower PLS intensity implies a low recombination rate of the electron-hole under light irradiation due to the migration of electrons to the surface of photocatalyst.[13,14] As depicted in Figure 4, it can be observed that the maximum of PLS emission peaks of the synthesised ZnO layers was found at 689 nm. However, the results show that the intensity of the PL spectra of the synthesised ZnO layer has a slightly decreasing order; hydrogen peroxide treated > heat treated > electrolysis. These results clearly indicate that the radiative recombination process will decrease when the thickness of the ZnO layer is increased.

### 3.2. Photocatalytic degradation of MB

The photocatalytic activity of the ZnO layer synthesised by different methods was assessed against MB degradation. The MB degradation was observed using UV-Vis spectrophotometer and with the initial dye concentration of 50 ppm, after 1 h incubation (almost

maximum percentage of photocatalytic degradation). The percentage of degradation was found in the order of ZnO synthesised by electrolysis (84%) > heat (79%) > hydrogen peroxide (65%), as shown in Figure 5(a).



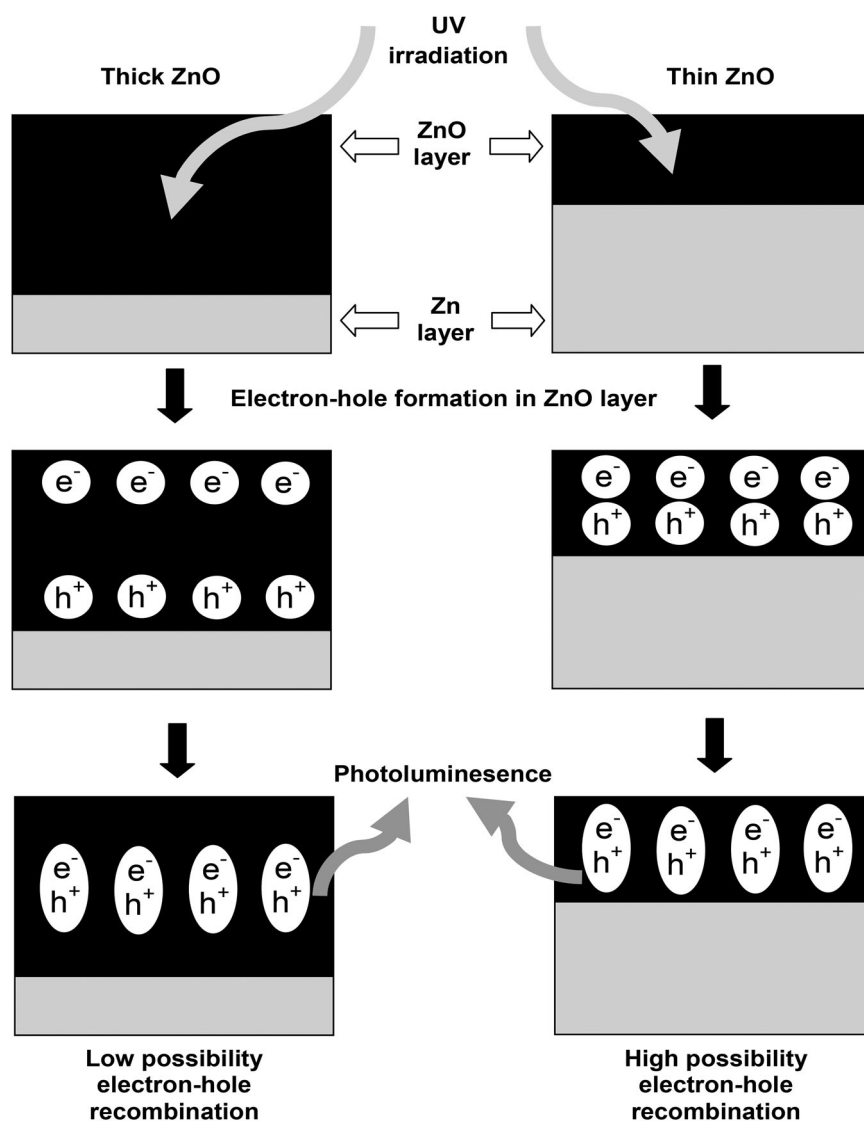
**Figure 5.** Photocatalytic degradation studies. (a) MB dye degradation by ZnO catalysts, (b) reusability and (c) photocatalytic stability.

Previously, ZnO has been used as photocatalysts for MB degradation under UV irradiation by various research groups. Flores et al. [15] reported 89% of MB ( $7.8 \times 10^{-6}$  M) degradation using 1.0 M of nanostructured ZnO particles synthesised by low-temperature air-assisted ultrasonic spray pyrolysis; however, the concentration of MB used to be lower than the present study. Pudukudy and Yaakob [16] observed complete degradation of MB using ZnO hexagonal nanogranules synthesised by solid state; nevertheless, the degradation reaction was performed with a high amount of catalyst for low MB concentrations at elevated temperatures. Kim and Park [17] observed that the efficient degradation of MB dye by rod-shaped ZnO is due to its increased absorption property. Delgado et al. [18] reported that the photocatalytic degradation of MB using ZnO prepared by the sol-gel method was achieved within 5 h. This variation in the rate of MB photocatalytic

degradation is due to the difference in the method used for synthesis, the size and surface area of the particle and the crystallinity of the catalyst. Compared with previous reports, ZnO catalyst synthesised by electrolysis and heat treatment methods shows higher MB degradation efficiency, and also the synthesis method is simple, fast and cost-effective.

### 3.3. Reusability and operational stability of synthesised ZnO catalyst

The reusability and operational stability of photocatalysts are important features for their practical applications. Therefore, MB degradation by synthesised ZnO catalysts by three different methods was assessed over several cycles. Figure 5(b) shows that fresh ZnO catalysts were able to degrade MB up to 84% (electrolysis), 79% (heat treatment) and 65% (hydrogen peroxide treatment)



**Scheme 1.** The electron-hole recombination in catalyst with thick and thin ZnO layers.



within 1 h of reaction time; however, in the repeated cycle all the samples required additional reaction time for the maximum percentage of degradation as achieved in the first cycle. Furthermore, it demonstrates the percentage of MB photocatalytic degradation by electrolysis and heat-treated ZnO was slowly decreased; whereas, in the case of hydrogen peroxide-treated ZnO, decreased within few repeated cycles. The slight decrease in photocatalytic activity might be due to the trace amount of MB dye and their degradation products absorbed on the surface of ZnO even after washing, which dampens the catalytic activity of ZnO. The photocatalytic stability result revealed that the half life of the ZnO layer synthesised by electrolysis, heat and hydrogen peroxide treatment was found up to sixth, fifth and third cycles, respectively (Figure 5(c)). It confirms that the recyclic applicability order of the synthesised ZnO layer was found to be electrolysis > heat > hydrogen peroxide treatment. Previous studies showed that the photocatalytic efficiency of ZnO decreased during the recyclic application.[19,20] Sanoop et al. [21] reported that 80% of yttrium-doped nanocrystalline ZnO photocatalytic activity was maintained after the fourth cycle in MB degradation. Interestingly, the ZnO layer synthesised by electrolysis and heat treatment maintained more than 75% and 66% of the photocatalytic efficiency even after the fourth cycle. Based on the SEM image in Figure 1, PLS emission peaks in Figure 4 and MB degradation results in Figure 5(a), it can be concluded that there is a correlation between photocatalytic activity for the degradation and thickness of the ZnO layer. Photocatalytic activity and their reusability were increased along with the increasing thickness of the ZnO layer on the surface of Zn plates. This might be due to the thickness of the ZnO layer consisting of a larger surface area and porosity; thus, providing enough space for the substrate and ligand interaction.

The electron-hole recombination in the catalyst with thick and thin ZnO layers is illustrated in Scheme 1. It shows that a high surface area might decrease the  $e^-/h^+$  recombination process due to impeding of the electron injection rate, as well as reducing the efficiency of the device by capturing the photo-generated molecule electrons in the ZnO layer; thus, enhancing the photocatalytic activity.[22,23] Finally, our results confirmed that electrolysis and heat-treated ZnO have considerable photocatalytic stability and anti-photocorrosive nature due to the thickness and enlarged surface layer.

#### 4. Conclusions

This investigation evaluated the three different methods for ZnO synthesis and confirmed that the ZnO layer

synthesised by electrolysis and heat treatment methods has efficient photocatalytic activity. The electrolysis and heat-treated ZnO layers had shown better operational stability and reusability. The thickness of the ZnO layer was directly associated with the photocatalytic activity of the catalyst; since with an increase of the ZnO layer,  $e^-/h^+$  recombination process will be decreased, thus resulting in the increase in photocatalytic activity. Finally, it can be proposed that both of the electrolysis and heat-treated ZnO might be a potential photocatalyst for AOPs-mediated pollutant remediation.

#### Disclosure statement

No potential conflict of interest was reported by the authors.

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#### References

- [1] Tünay O, Erdeml E, Kabdaşlı I, Ölmez T. Avanced treatment by chemical oxidation of pulp and paper effluent from a plant manufacturing hardboard from waste paper. *Environ Technol.* 2008;29:1045–1051.
- [2] Muruganandham M, Swaminathan M. Solar photocatalytic degradation of a reactive azo dye in TiO<sub>2</sub>-suspension. *Sol Energy Mater Sol Cells.* 2004;81:439–457.
- [3] Ling CM, Mohamed AR, Bhatia S. Performance of photocatalytic reactors using immobilized TiO<sub>2</sub> film for the degradation of phenol and methylene blue dye present in water stream. *Chemosphere.* 2004;57:547–554.
- [4] Ayyappan R, Neubert S, Mei B, et al. Enhanced performance of surface-modified TiO<sub>2</sub> photocatalysts prepared via a visible-light photosynthetic route. *Chem Commun.* 2012;48:8556–8558.
- [5] Abdollahi Y, Abdullah AH, Gaya UI, Zainal Z, Yusof NA. Enhanced photodegradation of o-cresol in aqueous Mn(1%)-doped ZnO suspensions. *Environ Technol.* 2012;33:1183–1189.
- [6] Yang LY, Dong SY, Sun JH, Feng JL, Wu QH, Sun SP. Microwave-assisted preparation, characterisation and photocatalytic properties of a dumbbell-shaped ZnO photocatalyst. *J Hazard Mater.* 2010;179:438–443.
- [7] Patil RS, Kokate MR, Shinde DV, Kolekar SS, Han SH. Synthesis and enhancement of photocatalytic activities of ZnO by silver nanoparticles. *Spectrochim Acta A Mol Biomol Spectrosc.* 2014;122:113–117.
- [8] Farbod M, Jafarpour E. Hydrothermal synthesis of different colors and morphologies of ZnO nanostructures and comparison of their photocatalytic properties. *Ceram Int.* 2014;40:6605–6610.
- [9] Li D, Huangn JF, Cao LY, Li JY, Yang HBO, Yao CY. Microwave hydrothermal synthesis of Sr<sup>2+</sup> doped ZnO

- crystallites with enhanced photocatalytic properties. *Ceram Int.* **2014**;40:2647–2653.
- [10] Shirzad Siboni M, Samadi MT, Yang JK, Lee SM. Photocatalytic reduction of Cr(VI) and Ni(II) in aqueous solution by synthesized nanoparticle ZnO under ultraviolet light irradiation: a kinetic study. *Environ Technol.* **2011**;32:1573–1579.
- [11] Anderson J, Chris GW. Fundamentals of zinc oxide as a semiconductor. *Rep Prog Phys.* **2009**;72:1–29.
- [12] Girtan M, Rusu GG, Dabos-Seignon S, Rusu M. Structural and electrical properties of zinc oxides thin films prepared by thermal oxidation. *J Appl Surf Sci.* **2008**;254:4179–4185.
- [13] Fujihara K, Izumi S, Ohno T, Matsumura M. Time-resolved photoluminescence of particulate TiO<sub>2</sub> photocatalysts suspended in aqueous solutions. *J Photochem Photobiol A: Chem.* **2000**;132:99–104.
- [14] Pozan GS, Kambur A. Significant enhancement of photocatalytic activity over bifunctional ZnO-TiO<sub>2</sub> catalysts for 4-chlorophenol degradation. *Chemosphere.* **2014**;105:152–159.
- [15] Flores G, Carrillo J, Luna JA, et al. Synthesis, characterization and photocatalytic properties of nanostructured ZnO particles obtained by low temperature air-assisted-USP. *Adv Powder Technol.* **2014**. doi.org/10.1016/j.appt.2014.02.004.
- [16] Pudukudy M, Yaakob Z. Facile solid state synthesis of ZnO hexagonal nanogranules with excellent photocatalytic activity. *Appl Surf Sci.* **2014**;292:520–530.
- [17] Kim SJ, Park DW. Preparation of ZnO nanopowders by thermal plasma and characterization of photo-catalytic property. *Appl Surf Sci.* **2009**;255:5363–5367.
- [18] Delgado GT, Romero CIZ, Hernandez SAM, Perez RC, Angel OZ. Optical and structural properties of the sol-gel-prepared ZnO thin films and their effect on the photocatalytic activity. *Sol Energy Mat Sol C.* **2009**;93:55–59.
- [19] Fu H, Xu T, Zhu S, Zhu Y. Photocorrosion inhibition and enhancement of photocatalytic activity for ZnO via hybridization with C60. *Environ Sci Technol.* **2008**;42:8064–8069.
- [20] Velmurugan R, Selvam K, Krishnakumar B, Swaminathan M. An efficient reusable and antiphotocorrosive nano ZnO for the mineralization of reactive orange 4 under UV-A light. *Sep Purif Technol.* **2011**;80:119–124.
- [21] Sanoop PK, Anas S, Ananthakumar S, Gunasekar V, Saravanan R, Ponnusami V. Synthesis of yttrium doped nanocrystalline ZnO and its photocatalytic activity in methylene blue degradation. *Arab J Chem.* **2012**. doi.org/10.1016/j.arabjc.2012.04.023.
- [22] Lai CW, Sreekantan S. WO<sub>3</sub> deposited TiO<sub>2</sub> nanotube arrays by thermal evaporation method for effective photocatalytic activity. *J Eng Sci.* **2012**;8:39–50.
- [23] Ríos-Valdovinos E, Amézaga-Madrid P, Antúnez-Flores W, Pola-Albores F, Pizá-Ruiz P, Miki-Yoshida M. Theoretical and experimental study of the photocatalytic activity of ZnO coated tubular reactor. *Mater Sci Eng B.* **2014**;179:41–47.