Simple fabrication of magnetically separable ZnO-based photocatalyst nanocomposites

ThianKhoon Tan1,*, PoiSim Khiew1, WeeSiong Chiu2 and ChinHua Chia3

1 Engineering Foundation, Faculty of Science and Engineering, University of Nottingham Malaysia, Jalan Broga, 43500 Semenyih, Selangor Darul Ehsan, Malaysia
2 Low Dimensional Materials Research Center, Department of Physics, Faculty of Science, Universiti Malaya, 50603 Kuala Lumpur, Malaysia
3 School of Applied Physics Studies, Faculty of Science & Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor Darul Ehsan, Malaysia
* E-mail: TK.Tan@nottingham.edu.my

Abstract. Magnetically recyclable ZnO/Fe3O4 nanocomposite photocatalyst was successfully fabricated through simple mechanical mixing and low calcination temperature. The nanocomposite was characterised by XRD, FESEM, TEM and EDX analysis. The magnetic nanocomposite optimisation, such as photocatalyst loading, doping amount of Fe3O4 nanoparticle into the nanocomposite and sintering temperature were conducted. The optimum loading amount of the ZnO/Fe3O4 nanocomposite was 9.0 wt%. The most favourable amount for Fe3O4 doped was 10 wt% and 300 °C was the value for the sintering temperature. The ZnO/Fe3O4 nanocomposite was successfully extracted by applying magnetic field and able to be reused with no significant change arises in the degradation efficiency.

1. Introduction
Water contamination has brought considerable threat to public health and ecosystems. This is due to the increasing demand of the toxic organic dyes by various industries such as textile, jute, paint and pharmaceuticals where they discharged their effluent into the environment without proper processes (Mandal, Dutta et al. 2019). There was report of more than 50% of current synthetic dyes are insusceptible to natural degradation (Muhd Julkapli et al. 2014). The accumulation of wastewater from these industries will definitely lead to significant damage that brought serious threat to the environment.

Current synthesis techniques such as green chemistry processes has been a highly promising technique due to its simple, mild chemical reaction and no toxic chemicals used. Lately, nano-sized semiconductors have been monopolised as photocatalytic oxidation processes due to their non-toxic and chemical properties (Fresno, Portela et al. 2014). There were also remarkable studies on the utilisation of visible light to successfully degrade variety of organic dyes in wastewater (Anwer, Mahmood et al. 2019). The frequently studied photocatalytic semiconductors are titanium dioxide (TiO2) and zinc oxide (ZnO). Recent research report ZnO shows better photodegradation performance for some dyes in aqueous solutions (Tudose and Suchea 2016). The performance of current photocatalysts are closely associated with low utilisation of visible light, wide energy bandgap and the duration of the electron-hole separation efficiency (Ge, Zhang et al 2019). While these major obstacles are constantly studied, to achieve high photocatalytic efficiency, another problem arises after the water was treated through photocatalytic processes. As a consequences, a simple and efficient technique to
separate and recycle the photocatalyst was by slotting magnetic materials into the photocatalyst (Kim, Woo et al. 2016). Fe₃O₄ was adopted in many magnetic photocatalysts due to its good magnetic properties, low cost and environmental friendly nature (Wu, Chen et al. 2019).

There have been extensive studies on various preparation methods in obtaining a remarkable and highly effective ZnO/Fe₃O₄ nanopowder. Wang et al. (2016) synthesised ZnO/Fe₃O₄ core/shell nanoparticle by simple two-step chemical method (Wang, Yang et al. 2016) whereas Nguyen et al. (2015) prepared ZnO/Fe₃O₄/CS magnetic nanocomposite with combination of ZnO nanoparticles and chitosan by co-precipitation method (Nguyen, Nguyen et al 2015). Another group of researcher have synthesized Fe₃O₄/CuO/ZnO/NGP using a sol-gel method followed by hydrothermal method for photodegradation of MB (Tju, Taufik et al. 2016). After thorough investigation, this study aims to present a cost effective method to synthesise ZnO based magnetic nanocomposites. After scrutinising few factors affecting photocatalytic efficiency, the separable ZnO/Fe₃O₄ magnetic nanocomposite photocatalyst was effectively degrade 97.3% of MB at 12 mg·L⁻¹ concentration.

2. Experimental

All the materials used in this study were of reagent grades. Zinc oxide (ZnO, R & M Chemicals), methylene blue (MB, R & M Chemicals) and iron oxide (Fe₃O₄, Systerm, ChemPur) were used directly without further purification. All solutions were prepared with Favorit Water Distiller deionised water.

In the preparation of ZnO/Fe₃O₄ magnetic nanocomposites photocatalyst materials, ZnO nanopowders was weighed followed by weighing of the Fe₃O₄ nanopowders. A different weight percentage (wt%) of Fe₃O₄ was prepared, i.e. 1, 5, 10, 12, 15 and 20 wt%. They were then placed in a porcelain bowl and were dry mixed for about 20 minutes. These premixed nanocomposites powders were then calcined for 5 hours for a set of sintering temperature, i.e. 200, 250, 300, 350, 400 and 450 °C, in the muffle furnace from Carbolite. The samples were calcined at the rate of 20 °C per minute. After calcined, the process was completed by grinding all samples with the micro spatula. This method is generally used to prepare mixed oxide catalyst material (Sun, Meng et al. 2019).

The resulting magnetic nanocomposites were confirmed by X-ray diffraction (XRD, Bruker) and the field emission scanning electron microscopy (FESEM, FEI) coupled with energy dispersive X-ray analyser (EDX). The morphologies were characterised by transmission electron microscope (TEM, LEO) and the specific surface area (BET) by using Micromeritics.

Distilled water was used to prepare various loading of the magnetic nanocomposites solutions, i.e. 1.0 wt% to 10.0 wt%, whereas MB dye in the range of 2.00 ppm to 12.0 ppm. 0.20 mL of the nanocomposites were immersed into 3.00 ml of the organic dye solution. These samples were placed in the UV chamber (Uvitec, CL-508.G) for various durations, at 10 minutes interval, to observe the capability of the nanocomposites to photodegrade the dye (Figure 1, Tan, Khiew et al. 2019).

After the irradiation, each nanocomposites samples were collected from the solutions by applying a magnetic field (0.6 T). A 2 mL aliquot of all samples were taken and placed into the UV-Visible Spectrophotometer (Varian, Cary 50). The scan rate was 120 nm/min through wavelength of 200 nm to 800 nm, where their absorption maximum was analysed and studied.

The Beer-Lambert law was applied when analysing the absorbance calibration curve of all the solutions (Mantele and Denize 2017). Therefore, the decolourisation efficiency was calculated by the equation: Percentage degradation (%) = \(\frac{[C_0 - C_f]}{C_0} \times 100 = \frac{[A_0 - A_f]}{A_0} \times 100\), where \(C_0\) and \(A_0\) are the dye concentration and the absorbance of the dye before irradiation, whereas \(C_f\) and \(A_f\) are the dye concentration and the absorbance of the dye after the irradiation of time \(t\).
3. Results and Discussion

3.1. Samples Morphologies for Different Sintering Temperature
This experiment was conducted on the ZnO/Fe$_3$O$_4$ nanocomposites for the 20 wt% doped Fe$_3$O$_4$.

3.1.1. FESEM Analysis. The prepared samples were sintered at 200, 250, 300, 350, 400 and 450 °C, respectively, for a duration of 5 hours. The FESEM micrographs of ZnO/Fe$_3$O$_4$ nanocomposites sintered at 300 °C is shown in Figure 1(a). The micrograph shows mixture of different particle size of nanoparticles but evenly distributed across the samples. In addition, all samples display moderate porosity which will contribute significantly to the surface area to initiate the degradation process.

Overall, the small spherical shapes particles are Fe$_3$O$_4$ particles whereas the medium and large rod-like and cubic shapes are ZnO particles. The particles surfaces are quite smooth, which shows no sign of over stressed was subjected onto the powder during mixing. The average particle size is (164 ± 12) nm for 300 °C sintering temperature. The results show no significant impact on the particle size for these range of sintering temperature.

3.1.2. XRD Analysis. Figure 1(b) shows XRD patterns for nanocomposites sintered at 200, 300 and 400 °C sintering temperatures. Samples main peaks at 31.8° of (100), 34.4° for (002) and 36.3° for (101) planes for ZnO, and at 30.2° for (220), 35.6° for (311) and 43.2° for (400) planes for Fe$_3$O$_4$ crystals, coincide with the hexagonal wurtzite phase for ZnO (space group P6$_3$mc; JCPDS 36-1451) (Nandi and Das 2019), and cubic single phase structure for Fe$_3$O$_4$ (face-centered cubic; JCPDS 82-1533) (Guy, Atacan et al. 2018). All samples’ peaks were quite similar with no unfamiliarity on the crystallinity of the nanocomposites. By using Scherer equation, the average crystallite size was calculated as (121 ± 13) nm for the 300 °C sintering temperature.

3.1.3. BET and EDX Analysis. The applied sintering temperature between 200 to 450 °C on the ZnO/Fe$_3$O$_4$ nanocomposites did not affecting the microstructure of the nanocomposites since the values averages for BET surface area and pore size were between 1.9 to 2.6 m$^2$/g. On the other hand, the EDX spectrums of ZnO/Fe$_3$O$_4$ nanocomposites for 300 and 400 °C sintering temperature acquired the elemental map which conclude Fe$_3$O$_4$ nanoparticles were deposited on the surface of the ZnO/Fe$_3$O$_4$ nanocomposites (Amornpitoksuk, Suwanboon et al 2018). Thus, the XRD results conformed with the EDX that high crystallinity single phase structure was form.

3.2. Samples Morphologies when Doped with Different wt% of Fe$_3$O$_4$
This experiment was conducted on the ZnO/Fe$_3$O$_4$ nanocomposites sintered at 300 °C.

3.2.1. FESEM Analysis. Figure 1(c) shows the micrographs for the ZnO/Fe$_3$O$_4$ nanocomposite samples with 10 weight percent (wt%) of Fe$_3$O$_4$. The image shows mixtures of obviously many different particles of various sizes but evenly scattered all around. The small particles are spherical and slightly mixed with elongated structures, while the larger particles are of cubic and rod shapes. The particles are fairly distributed without detectable agglomeration but high porosity was seen all around. The average particle size for 10 wt% doped Fe$_3$O$_4$ is (159 ± 12) nm.

3.2.2. XRD Analysis. Figure 1(d) is the XRD results for the ZnO/Fe$_3$O$_4$ nanocomposites with 20, 10 and 1 weight percent (wt%) of Fe$_3$O$_4$ nanoparticles. The diffraction main peaks at 31.8° of (100), 34.4° for (002) and 36.3° for (101) planes of wurtzite crystal structure for ZnO standard JCPDS (No. 36-1451), whereas peaks at 30.2° for (220), 35.6° for (311) and 43.2° for (400) planes of cubic single phase structure for Fe$_3$O$_4$ crystals for JCPDS (No. 82-1533). These basically explained that ZnO and Fe$_3$O$_4$ nanoparticles samples are well mixed by the dry mixing. The average crystallite size as calculated by using the Scherer equation is (137 ± 15) nm for the 10 wt% of doped Fe$_3$O$_4$ nanocomposite sample.
3.2.3. **BET and EDX Analysis.** BET and pore size results for 10 wt% doped Fe$_3$O$_4$ is 1.676 and 22.62, respectively. No significant changes were detected in the BET result if compared to the undoped ZnO nanoparticles, except for the 10 and 1 wt% doped samples. Nonetheless, the increase of these pores would certainly contribute to the photocatalytic performance. EDX results acquire the peaks of O, Zn and Fe elements for the nanocomposites which conformed Fe$_3$O$_4$ mixed well with ZnO. These EDX and XRD analysis can definitely verified the purity of the prepared nanocomposites.

3.3. **Transmission Electron Microscopy (TEM) Analysis**

Figure 2(a) provides the TEM film for the 10 wt% doped Fe$_3$O$_4$ sintered at 300 °C for the ZnO/Fe$_3$O$_4$ nanocomposites. The micrograph result shows the shape of the nanocomposite was inconsistent with elongated and cubic structures but without any agglomeration. The average particle size obtained from the particle size distribution was $(162 \pm 12) \text{ nm}$.

3.4. **The Study of Photocatalytic Effects**

Extensive studies have been placed on the effects of photocatalyst loading for the degradation of organic dyes in wastewaters (Chanu, Singh et al. 2019). For this study, the photocatalysts loading was conducted in the range of 1.0 to 10.0 wt% by using MB dye at 12.0 ppm concentration.

3.4.1. **ZnO/Fe$_3$O$_4$ Loading.** Figure 2(b) depicts degradation rate increases with the catalyst loading to 0.1593 min$^{-1}$ for 9.0 wt% but dropped to 0.1574 min$^{-1}$ for 10.0 wt% catalyst. This was due to higher loading tends to increase the surface area which relate to the active sites and consequently improve degradation rate (Habibi-Yangjeeh and Shekofteh-Gohari 2016). The rate dropped due to increase of cloudiness of the solution, which bring blockage to light absorption thus affecting the photocatalytic process (Han, Wang et al. 2012). The kinetic constant for MB follows pseudo-first-order kinetics from Langmuir-Hinshelwood (LH) model, which can be described by $\ln(C_0/C) = kt$, where $C_0$ and $C$ are the initial and actual concentration of MB and $k$ is the degradation rate parameter.

3.4.2. **Different Sintering Temperature.** Kinetic analysis for Figure 2(c) shows all ZnO/Fe$_3$O$_4$ nanocomposite samples attributed to the LH model and coincide with the pseudo-first-order kinetics. The highest kinetic rate recorded was sample calcined at 300 °C. This result could relate to its highest pore volume and pore size as compared to other samples sintered at different temperature.

3.4.3. **Different wt% of Fe$_3$O$_4$.** Figure 2(d) shows highest degradation rates $k$, for samples with 1 wt% to 10 wt% Fe$_3$O$_4$ doped nanocomposite material irradiated in just 30 minutes. This results indicated
that current amount of doped Fe₃O₄ nanoparticles was not affecting the photocatalytic performance of ZnO nanoparticles (Bhukal, Shivali et al. 2014). This clarified that the doping of Fe₃O₄ nanoparticle was within its acceptable range that can hinder the reactive surface area of the ZnO nanoparticle (Han, Liao et al. 2012).

3.5. The Magnetic and Reliability Analysis

The photocatalyst loading of 9.0 wt% ZnO/Fe₃O₄ nanocomposite with 10 wt% doped Fe₃O₄ sintered at 300 °C was conducted with the MB dye.

3.5.1. Vibrating Sample Magnetometry Analysis (VSM). Figure 3 provides the magnetization curves versus the magnetic field for ZnO nanoparticle and ZnO/Fe₃O₄ nanocomposite. Obviously ZnO nanoparticle is diamagnetic material since no magnetic properties was displayed, whereas for ZnO/Fe₃O₄ nanocomposite, apparent magnetic hysteresis loops with ferromagnetic feature was formed, which is obviously a soft ferromagnetic material. This feature was coincide with the finding by Guy et al. (2018) on various ZnO based nanocomposites photocatalysts which also found ferromagnetic feature for their ZnO/Fe₃O₄ nanocomposite (Guy, Atacan et al. 2018). The magnetic moments were simply induced by the magnetic field due to the minimal coercivity revealed by the samples. The ZnO/Fe₃O₄ nanocomposite was easily magnetised achieving 84% induced magnetization with only 1088 Oe magnetic field. The ZnO/Fe₃O₄ nanocomposite saturation magnetization was 6.124 emu/g.

![Figure 3](image-url) Hysteresis loop for ZnO (ZnO) and ZnO/Fe₃O₄ (ZnF) nanocomposite powders.

![Figure 4](image-url) Separation of ZnO/Fe₃O₄ powder by applying a magnetic field.

3.5.2. Magnetic Separation Analysis. The magnetically induced separation experiment for 9.0 wt% loading of ZnO/Fe₃O₄ nanocomposites is shown in Figure 4 by applying a magnetic field strength of 0.6 T. The effect of the magnetically induced separation is clearly visible with the progressive separation of a colloidal suspension. After the magnetic separation, the colloidal ZnO/Fe₃O₄ nanocomposites remain dispersible without manifestation of irreversible agglomeration.

3.5.3. Repeatability Analysis. The repeatability analysis was performed under the similar experimental conditions. After the first run of the photodecomposition was completed, the retrieved nanocomposite was reused for the following analysis, where it was recycled for at least three runs. Based on the results, no significant changes appear in degradation efficiency with an average of 97% percentage degradation.

4. Conclusion

Novel magnetically separable ZnO/Fe₃O₄ nanocomposite photocatalyst was successfully prepared. The ZnO/Fe₃O₄ nanocomposite photocatalyst has been carefully inspected by having the optimum loading of 9.0 wt%, 10 wt% of doped Fe₃O₄ and 300 °C of sintering temperature. The synthesised nanocomposite was equally superior in the effectiveness to photodegrade organic dye as compared to
its counterpart. The nanocomposite was recycled for three times and achieved the same degradation effect.

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