Fabrication of Flower-like ZnO Micro/Nanostructures for Photodegradation of Pre-treated Palm Oil Mill Effluent

Sze-Mun Lam1*, Kok-Ann Wong1 and Jin-Chung Sin2

1 Department of Environmental Engineering, Faculty of Engineering and Green Technology, Universiti Tunku Abdul Rahman, Jalan Universiti, Bandar Barat, 31900 Kampar, Perak, Malaysia
2 Department of Petrochemical Engineering, Faculty of Engineering and Green Technology, Universiti Tunku Abdul Rahman, Jalan Universiti, Bandar Barat, 31900 Kampar, Perak, Malaysia

*Email: lamsm@utar.edu.my

Abstract. Flower-like ZnO micro/nanostructures were fabricated by a simple and surfactant-free reflux method. X-ray diffraction findings showed that the prepared ZnO product was highly crystallite with hexagonal wurtzite structure. The band gap energy of ZnO sample was measured to be 3.18 eV via an optical reflectance spectrum. The flower-like morphological features of ZnO micro/nanostructures were witnessed through field-emission scanning electron microscopy. Such micro/nanoparticles could be used in the photodegradation of pre-treated palm oil mill effluent (POME) under UV irradiation.

1. Introduction

To date, search suitable and sustainable pollution-degradation strategies become paramount important to circumvent the environmental problems. Particularly, Malaysia as one of the largest water polluters originates from oil palm industries. It is a well-known that fresh POME is acidic with the pH ranging from 4 to 5, chemical oxygen demand (COD) of 40,000–100,000 mg/L and biological oxygen demand (BOD) of 25,000–65,000 mg/L [1–3]. Direct release of palm oil mill effluent (POME) causes severe environmental pollution [1,2]. The traditional POME treatment in Malaysia is through aerobic ponding system. However, there were some shortcomings of this treating method including land consuming and long retention time (up to months).

An alternative approach, light irradiation/semiconductor technology has been recently demonstrated for POME degradation [3–5]. This technique employs light energy as an activating agent for photocatalyst light absorption and initiated a series of active radicals generation for photo-mineralization of organic compounds. ZnO is a semiconductor which is extensively studied for a myriad of applications such as hydrogen-evolution, air pollution control and water treatment and others, attributed to its unique electrical, optical and mechanical properties [5,6]. Due to its saline features, a myriad of wet chemical technique including co-precipitation, sol-gel, hydrothermal techniques and some wet-chemical solution processes have been widely utilized to fabricate various ZnO nanostructures. It is well known that the nanoscale photocatalyst is anticipated to improve photocatalytic performance because of a larger specific surface area and more surface contact sites for the process [7]. Among these available techniques, reflux method is a facile, cheap, effective method...
and most importantly it can be conducted at short periods, normal pressure and at room temperature. Despite this method has been used to prepare the ZnO nanoparticles, its ability to form different structures at adequately huge amounts for practical applications including photocatalysis still deserves to be investigated.

In the present study, flower-like ZnO micro/nanoparticles has been fabricated by a reflux technique at low temperature (~65°C). The ZnO micro/nanoparticles were then characterized by various characterization techniques such as X-ray diffraction, field emission-scanning electron microscopy, energy dispersive X-ray spectroscopy, Fourier transform infrared spectroscopy and UV–vis diffuse reflectance spectroscopy measurements. The photocatalytic activity of ZnO micro/nanoparticles were evaluated in pre-treated POME under UV irradiation.

2. Experimental

All chemicals were in analytical grade and used as-purchased without further purification. Distilled water (DI) was utilized during the study. Pre-treated POME was collected from a palm oil mill factory positioned in Air Kuning, Perak Malaysia and stored in 4°C freezer.

2.1. Preparation of ZnO micro/nanoflowers

Zn(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O (0.1 M) was first prepared in 100 mL distilled water and stirring continuously for 20 min. The mixture was then slowly added into NaOH (0.1 M) solution under magnetic stirring. The final pH value of solution was adjusted to 12.12 by addition of extra NaOH. Subsequently, the mixed suspensions were heated and refluxed 60°C for 8 h and cooled to room temperature naturally. The as-formed products were filtered, washed with distilled water and ethanol and dried at room temperature.

2.2. Characterization

The samples were analyzed by X-ray diffraction (XRD) pattern recorded using a Philips PW1820 diffractometer with Cu Kα radiation at a scanning rate of 2° min\textsuperscript{-1} in the range of 20°–80°. The morphology of the samples was scanned using a Quanta FEG 450 field emission-scanning electron microscope (FESEM) with an energy dispersive X-ray spectroscopy (EDX) analysis. UV–vis diffuse reflectance spectroscopy (DRS) spectrum was recorded on a Perkin Elmer Lambda 35 UV-vis spectrophotometer with BaSO\textsubscript{4} as a reference. The infrared spectrum was tested using a Thermo scientific Nicolet IS10 Fourier Transform Infrared (FTIR) spectrometer at scanning range from 500 to 4000 cm\textsuperscript{-1}. Photoluminescence (PL) spectroscopy was conducted at room temperature using a Perkin Elmer Lambda S55 spectrofluorometer using a Xe lamp with an excitation wavelength of 315 nm.

2.3. Photocatalytic test

All experiments were carried out in an immersion well photoreactor with dimensions 200 × 100 × 60 mm (height × outer diameter × inner diameter). In the center of the photoreactor, a 15 W UV Pen-Ray lamp with maximum emission at approximately 254 nm was used as UV source. The total UV output intensity at distance of 10 mm from the UV light, used by measure of a radiometer was 5400 μW/cm\textsuperscript{2}. The reaction mixture was prepared by adding 400 mg catalyst to the photoreactor containing 400 mL of pre-POME solution. Before the photoreaction, the pre-POME solution was magnetically stirred in the dark for 1 h. It was then irradiated and bubbled with air at a fixed flow rate of 3 mL/min. At different time intervals, 5 mL of the solution was withdrawn and centrifuged immediately to separate the suspended solids. The filtrate was then analyzed by COD, BOD\textsubscript{5}, total suspended solid (TSS), oil and grease, turbidity, colour and pH in according to the standard methods of the American Public Health Association (APHA) [8]. The COD was determined using a Hach DRB200COD reactor after 2 h of digestion at 423 K. To analyze BOD\textsubscript{5}, the samples were subjected to an incubator for 5 days at 298 K. Prior to the incubation, 10 mL of samples were diluted to 300 mL with deionized water. The dissolved oxygen (DO) for BOD\textsubscript{5} was taken before and after the incubation process. The BOD\textsubscript{5} value can be calculated as shown in Equation (1):

$$\text{BOD}_5 \text{ (mg/L)} = (\text{DO}_1 - \text{DO}_2)/P$$  \hspace{1cm} (1)
where $DO_1$ and $DO_2$ are the initial and final DO values, respectively and $P$ denotes as the dilution factor. In addition, the turbidity was measured using a Lovibond Turbicheck turbidimeter and expressed in Nephelometric Turbidity Unit (NTU). The TSS was determined according to 8006 Photometric method [9] using an UV-Vis spectrophotometer. The TSS content was expressed in mg/L.

The colour of the sample was also determined using an UV-Vis spectrophotometer according to a colorimetric platinum cobalt method as measured in platinum cobalt (Pt-Co) unit. To study the oil and grease content in pre-treated POME, three doses of hexane extraction was performed on 30 mL of pre-treated POME sample and evaporated in water bath at 60°C. The weight of round bottom flask before and after evaporated was recorded and the difference between the weights was the oil and grease content in pre-treated POME sample. The solution pH of the sample was tested using a HANNA Instruments HI2550 pH meter. In order to determine the reproducibility of the results, at least duplicated runs were carried out for each condition for averaging the results and the experimental error was found to be within ±4%.

3. Results and discussion

Figure 1a displays the XRD pattern of the as-prepared ZnO product. All of the diffraction peaks were labelled and could be matched with hexagonal wurtzite phase of ZnO (JCPDS Card file No. 36–1451) [10,11]. The strong and sharp XRD peaks in the figure demonstrated that the as-prepared ZnO were highly crystallinity. Further confirmation of formation of ZnO sample obtained from the EDX analysis. The presence of Zn and O peaks can be simply found in Figure 1b. The elemental carbon (C) detected was came from the supporting carbon tape. The UV–vis DRS spectrum of the ZnO product (Figure 1c) depicted a steep absorption edge which lay around 400 nm without any other absorption peak. The obtained region was a characteristic region for the absorption band of the hexagonal phase of ZnO [9,11]. The band gap energy of the ZnO sample can be acquired from the plot of $(F(R)hv)^{0.5}$ versus photon energy ($E$). The band gap energy was measured to be 3.18 eV (inset of figure 1c), which was concordance with the reported ZnO catalyst [12].

Figure 1d presents FTIR spectrum of as-prepared ZnO products. The emergence of distinctive absorption band around ~500 cm$^{-1}$ could be related to Zn–O stretching vibrations. A distinct band appearing around 898 cm$^{-1}$ in the samples can be assigned to the nitrate (NO$_3^-$) ion groups. Moreover, a weak band at 1620 cm$^{-1}$ could be corresponded to bending modes of O–H vibration, whereas an intense broad band at around 3410 cm$^{-1}$ for the samples can be attributed to O–H stretching vibration [13,14]. These FTIR results confirmed that ZnO micro/nanoflowers possessed hexagonal structures, which was in agreement with the results of XRD (figure 1a).

FESEM analysis of as-prepared ZnO products was carried out under different magnifications. Figure 2a shows the production of flower-like ZnO micro/nanostructures with high yield. The sizes of the products were quite uniform and varied from 800 nm to 2.6 μm. The magnified image in figure 2b indicated that flower-like micro/nanostructure with several petals growing radially from the center. Thus, a simple, cost-effective and surfactant-free chemical solution technique was successfully used to produce a large amount synthesis of 3D ZnO micro/nanostructures in this work.

The photoactivity of as-prepared ZnO samples was examined by degrading pre-treated POME under UV light irradiation. Figure 3 shows that the POME solution was degraded about 96.0% by ZnO micro/nanoflowers under 120 min irradiation time. Further experiments were conducted to examine the photoactivity of photocatalysts. When the solution with the micro/nanoflowers was kept in the dark or when the solution was irradiated without the ZnO micro/nanoflowers, only small amounts of pre-treated POME were adsorbed or degraded. The degree of pre-treated POME degradation of the two experiments attained 2.1% and 18.8%, respectively under 150 min irradiation time. Under similar conditions of UV light irradiation, the ZnO micro/nanoflowers indicated much greater activities that of commercial ZnO (63.0%). It inferred that the as-prepared ZnO samples were active photocatalysts. Other measured water quality parameters of the pre-treated POME for both before and after the ZnO photocatalytic treatment are shown in Table 1. It can be found that the BOD5, turbidity, TSS, colour
and oil and grease removal efficiencies were 64.8%, 85.1%, 78.9%, 80.5% and 58.1%, respectively. The final pH of the treated POME was found to decrease from pH 8.65 to pH 8.60.

Figure 1. (a) XRD pattern, (b) EDX spectrum, (c) UV-vis DRS spectrum and (d) FTIR spectrum of ZnO micro/nanoflowers. Inset of (c) is the plot of $(F(R)hv)^{0.5}$ vs $E(hv)$.

Figure 2. FESEM images of ZnO micro/nanoflowers at different magnifications (a) 2,000x and (b) 20,000x.

Figure 3. Pre-treated POME degradation dependence on irradiation time at different conditions.
Table 1. Summary of measured pre-treated POME quality parameters before and after ZnO photocatalytic treatment.

| Parameter                | As-received pre-treated POME | After 120 min UV light | Removal efficiency (%) |
|--------------------------|------------------------------|------------------------|------------------------|
| COD (mg/L)               | 50                           | 2                      | 96.0                   |
| BOD₅ (mg/L)              | 54                           | 14                     | 64.8                   |
| Turbidity (NTU)          | 1.75                         | 1.49                   | 85.1                   |
| Colour (Pt-Co)           | 128                          | 27                     | 78.9                   |
| TSS (mg/L)               | 41                           | 8                      | 80.5                   |
| Oil and grease (mg/L)    | 0.43                         | 0.18                   | 58.1                   |
| pH                       | 8.65                         | 8.60                   | –                      |

4. Conclusion
Flower-like ZnO micro/nanostructures were successfully synthesized via a reflux route at low temperature of 65°C. The proposed method was facile and suitable to yield a large fabrication of ZnO micro/nanoflowers. The physico-chemical and optical properties of the as-prepared ZnO micro/nanoflowers were confirmed by XRD, FESEM, EDX, FTIR and UV–vis DRS analyses. The ZnO micro/nanoflowers have displayed good photocatalytic performance for the pre-treated POME degradation under UV irradiation. The removal efficiencies of other water quality parameters such as BOD₅, turbidity, TSS, colour, oil and grease and pH were also obtained.

Acknowledgements
This work was supported by the Universiti Tunku Abdul Rahman (UTARRF/2016–C2/S03 and UTARRF/2017–C1/L02) and Ministry of Higher Education of Malaysia (FRGS/1/2015/ TK02/UTAR/02/2 and FRGS/1/2016/TK02/UTAR/02/1).

References
[1] Bello M M, Nourouzi M M, Abdullah L C, Choong T S Y, Koay Y S and Keshani S 2013 J. Hazard. Mater. 262 106
[2] Poh P E and Chong M F 2009 Bioresour. Technol. 100 1
[3] Cheng C K, Derahman M R and Khan M R 2015 J. Environ. Chem. Eng. 3 261
[4] Ng K H, Lee C H, Khan M R and Cheng C K 2016 Chem. Eng. J. 286 282
[5] Ng K H and Cheng C K 2016 Chem. Eng. J. 300 127
[6] Lam S M, Sin J C, Abdullah A Z and Mohamed A R 2012 Desalin. Water Treat. 41 131
[7] Tian Y L, Chang L L, Lu J L, Fu J, Xi F N and Dong X P 2013 ACS Appl. Mater. Interfaces 5 7079
[8] APHA, AWWA, WPCF 2005 21st ed. American Public Health Association, Washington, D.C., USA
[9] Bakraouy H, Souabia S, Diguada K, Dkhissia O, Sabarb M and Fadil M 2017 Proc. Saf. Environ. 109 621
[10] Sin J C, Lam S M, Satoshi I, Lee K T and Mohamed A R 2014 Appl. Catal. B: Environ. 148–149 258
[11] Sin J C and Lam S M 2016 Mater. Lett. 182 223
[12] Karman T and Selvakumar S A S 2016 J. Mol. Struct. 1125 358
[13] He J, Luo Q, Cai Q Z, Li X W and Zhang D Q 2011 Mater. Chem. Phys. 129 242
[14] Lam S M, Sin J C Abdullah A Z and Mohamed A R 2013 J. Mol. Catal. A: Chem. 370 123