

# One-step Production of Biodiesel through Simultaneous Esterification and Transesterification from Highly Acidic Unrefined Feedstock over Efficient and Recyclable ZnO Nanostar Catalyst

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## ABSTRACT

Zinc oxide (ZnO) nanostar synthesized by simple and up-scalable microwave-assisted surfactant free hydrolysis method was applied as catalyst for biodiesel synthesis through one-step simultaneous esterification and transesterification from high free fatty acid (FFA) contaminated unrefined feedstock. It was found that ZnO nanostar catalyst was reacted with FFA to yield zinc oleate (ZnOl) as intermediate and finally became zinc glycerolate (ZnGly). With the re-deposition of ZnGly back to the ZnO nanostar catalyst at the end of the reaction, the catalyst can be easily recovered and stay active for five cycles. Furthermore, the rate of transesterification is highly promoted by the presence of FFA (6 wt.%) which makes it an efficient catalyst for low grade feedstock like waste cooking oil and crude plant oils.

## Keywords

biodiesel • free fatty acid • simultaneous esterification and transesterification • zinc oxide

## Highlights

- The ZnO nanostar can be applied in one-step biodiesel production from unrefined feedstock.
- Higher degree of FFA containing feedstock could affect the rate of transesterification.
- The ZnO nanostar was found to react with oleic acid to form ZnOl and finally became ZnGly.
- The ZnO nanostar served not only as a catalyst, it was also a catalyst support.

## 1. Introduction

Owing to the limiting storage of fossil fuel and the serious environment problems, exploration of sustainable liquid fuel has become an important research area to sustain human life. Biodiesel is found to be one of promising renewable, non-toxic, carbon neutral, low sulphur content and environmentally friendly fuel. It may curtail the harmful emission such as NO<sub>x</sub>, SO<sub>x</sub>, CO, CO<sub>2</sub>, unburnt hydrocarbon and particulates [1-4]. The transesterification reaction involved the conversion of triglyceride into FAME is one of the chemical reactions for biodiesel synthesis and has widely been used to reduce the viscosity of triglycerides [1,2,4]. Homogeneous strong acid (e.g. H<sub>2</sub>SO<sub>4</sub> or HCl) and strong base (e.g. NaOH or KOH) are commonly employed as catalyst for a classical production of biodiesel, however,

large amount of fresh water is necessary to purify the FAME product which is straightly restricted by two international standard of ASTM D6751 and EN 14214.

In view of this, more environmentally friendly heterogeneous catalysts employed for transesterification are getting more and more attention since the solid catalyst can easily be recovered. Alkaline earth metal oxides and hydroxides [5-9], various alkali metal supported on alumina [10-13], mixed alkaline earth metal-transition metal oxide [14], hydrotalcites [15], zeolite [16], silica-supported oxide [17] and tetraalkylammonium hydroxides immobilized SBA-15 [18] act as the heterogeneous base catalysts for biodiesel synthesis which have been widely studied and reported in literature. Moreover, the price of biodiesel is much higher than that of commercial diesel fuels because of the expensive cost of feedstock. Relatively cheaper and higher degree of free fatty acid (FFA) and water containing feedstock become more famous to be used.

Zinc oxide (ZnO), is one of the amphoteric transition metal oxide that can effectively catalyze both esterification of FFA and transesterification of triglycerides. Wide range of feedstock such as rapeseed oil [19], soybean oil [20,21] and plam oil [22] can be applied in the ZnO catalyzed biodiesel production with noteworthy catalytic conversion. Some of the literatures reported that ZnO catalyzed transesterification was performed at high temperature ( $>200\text{ }^{\circ}\text{C}$ ) and under a high pressure [19-21] while some of reports discussed that the catalytic reaction was carried out at mild methanol refluxing temperature [22]. This is an interesting area to investigate the influence of feedstock composition and the main role of ZnO as well as the potentiality for the generation of intermediate and side product during the catalytic transesterification and simultaneous esterification and transesterification reactions as this investigation has not been reported so far.

This present study reported the isolation and characterization of zinc oleate (ZnOl) intermediate and side product zinc glycerolate (ZnGly) after successive application of ZnO catalyst in catalytic transesterification and one-step simultaneous esterification and transesterification reactions. Reinoso et al. studied that the utilization of ZnGly [23] and zinc carboxylates [24] as an effective catalyst towards catalytic transesterification and simultaneous esterification and transesterification at a reaction temperature of  $140\text{ }^{\circ}\text{C}$  with a high feedstock conversions ( $>80\%$ ) obtained in 2 hours. Furthermore, a unique star-like ZnO catalyst was synthesized by microwave-assisted solvent free hydrolysis and applied as a target catalyst for the catalytic reactions from high FFA contaminated feedstock and catalyst support for deposition of side product due to high surface area of special star-like feature, enhancing its stability and robustness. This unique morphology exhibits a higher surface area which is beneficial for the characterization of morphological changes by electron microscopy.

## 2. Experimental

### 2.1. Materials

Crude rice bran oil and refined food grade canola oil were purchased from local store in China and Hong Kong respectively. Crude *Jatropha* oil was collected through in-house cold-pressed oil extractor using *Jatropha* seed obtained from local store in China. Cold-pressed *Camelina* seed oil was obtained from Campressco Products Inc. (Saskatchewan, Canada). Oleic acid (99.9 %) and glycerol (99.6 %) were obtained in laboratory reagent grade and analytical reagent grade respectively from Fisher Chemical. Zinc nitrate hexahydrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 98 %) and phenolphthalein were supplied by Acros and Sigma Aldrich respectively. Methanol (99.8 %), ethanol (99.0 %) and diethyl ether (99.5 %) were obtained in ACS reagent grade. Aqueous ammonia solution (28.0 – 30.0 wt.%), potassium

hydroxide (KOH) and sodium hydroxide (NaOH) were purchased from UNI-CHEM. Zinc acetate dihydrate ( $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ , >98 %) was purchased in laboratory reagent grade from BDH Chemical Ltd.

## 2.2. Catalyst preparation and characterization

### 2.2.1. Catalysts preparation

ZnO nanostar was synthesized by solvent free hydrolysis with an assistance of microwave irradiation. No calcination step is needed and similar preparation route has been reported by Cho et al. [25]. Aqueous ammonia water (0.16 M) was added into the transparent zinc salt solution which is prepared by dissolving  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  (330 mg) in milli-Q water (150 mL). The solution was then heated immediately using a microwave synthesis system (Micro SYNTH) at a fixed temperature of 80 °C with a fixed microwave power of 400 W for 30 min. The mother liquid was decanted and the white precipitate was washed by milli-Q water and ethanol three times, and finally dried at 80 °C.

ZnGly nanoplate was synthesized with referenced to the procedure reported by Dong and coworker [26] with some modifications. A solution of  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  in glycerol (50 mL) containing milli-Q water (1 mL) was prepared under a flow of  $\text{N}_2$  for 15 min. The reaction mixture was heated under reflux at 160 °C for 1 h. The mother liquid was poured out and the white precipitate was washed with milli-Q water and ethanol three times, and finally dried at 80 °C.

ZnOI was followed by Reinoso et al. [24] with some modifications. Stoichiometric ratio of oleic acid (1 g) and NaOH (142 mg) were added into milli-Q water (35 mL) at 60 °C with constant stirring for 30 min. Zinc salt solution prepared by dissolving the  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (523 mg) in milli-Q water (10 mL) and then added into reaction mixture in drop-wise manner. The reaction mixture was stood for a vigorous stirring for further 1 h. The white precipitate was isolated out by centrifugation, washed with milli-Q water followed by ethanol three times and dried at 80 °C.

### 2.2.2. Catalyst characterization

The morphology of the catalysts were characterized by a Hitachi S-4800 field emission scanning electron microscope (SEM) operating at 5 kV equipped with associated energy dispersive spectrometry (EDX) with Horiba EMAX EDS detectors and a JEOL Model JEM-2100F field emission transmission electron microscope (STEM) operating at 200 kV. Powder X-Ray diffraction (XRD) patterns were collected by a Rigaku SmartLab X-ray Diffractometer using a  $\text{CuK}\alpha$  ( $\lambda = 1.54056 \text{ \AA}$ , 45 kV, 200 mA) radiation with  $2\theta$  in ranged from 10° to 80° in a step size of 0.02°. Solid infrared (IR) spectra of sample catalysts pressed in KBr pellets were obtained by Nicolet 380 FTIR spectrometer in ranging from 400 to 4000  $\text{cm}^{-1}$ . The elemental composition on the catalyst surface was characterized using Axis Ultra DLD X-ray photoelectron spectroscopy (XPS) equipped with monochromatic Al-K $\alpha$  radiation of 1486.6 eV and with an electron take off angle of 90°. The pressure in sample chamber was kept at  $10^{-8}$  Torr during analysis. All binding energies were referenced to peak of C 1s of 285.0 eV.

## 2.3. Feedstock evaluation

With reference to ASTM D664, a standard titration method with a titrant of standard KOH solution was applied in determination of the acidity (AD) and acid value (AV) for all feedstock. A feedstock sample (around 0.3 g) was added in a solvent mixture of absolute ethanol and diethyl ether (5 mL, 1 : 1 v/v) and approximately few drops of methanolic phenolphthalein solution were added as indicator for end point detection. The analyte was titrated against KOH solution (0.01 N) with a vigorous shaking until the pale pink colour is observed. The quantity of water in each feedstock

was estimated by Karl Fischer titration based on ASTM D4377 by using an automated V20 Volumetric Karl-Fischer Titrator. A list of feedstock samples as shown in Table 1 are often employed as a raw material for biodiesel synthesis, especially for the unrefined feedstock. Unrefined feedstock may serve as a replacement to the refined plant oil which lower the production cost. The fatty acid content and acid value of various feedstock are generally ranged from 0.11 to 4.93 wt.% and from 0.22 to 9.78 mg<sub>KOH</sub>/g. The fatty acid profiles and its composition of feedstock including refined canola oil and unrefined oils and waste cooking oil are investigated by GC-FID as summarized in Table 2. It is found that all feedstock are having the fatty acid chain length of 16 to 22 which is desirable for biodiesel synthesis. The fatty acid chains of triglycerides vary from each other in the location and the number of double bonds which govern the boiling point of the FAME.

## 2.4. Catalytic reaction for biodiesel production

The catalytic transesterification and simultaneous esterification and transesterification reactions were carried out in a stirred batch reactor. The reaction mixture containing feedstock (0.46 g), methanol (0.6 mL) and the catalyst (36.8 mg) was heated at 140 °C with a constant stirring at 750 rpm for pre-designed time. When the catalysis was completed, the reaction mixture was isolated out and the catalytic conversion was calculated according to the Equation 3 using <sup>1</sup>H-NMR spectroscopy (Bruker, 400 MHz) with CDCl<sub>3</sub> [27]. The reaction was allowed to cool down to room temperature after completion of the catalytic reaction. The used catalyst was isolated out and was dried at room temperature for the next cycle of catalytic reaction without any washing steps. The same amount of fresh feedstock and methanol were added to the recycled catalyst and the catalytic study was performed for several cycles under the same conditions. By the spike recovery, the analytical method has been validated to show a deviation within 5 % to the original spiking concentration. Therefore, all feedstock conversions were estimated to show an error of ±5 %.

## 3. Results and discussion

### 3.1. Catalyst characterization

As shown in Fig.1a, the as synthesized ZnO is exhibiting a star-like morphology with average particle size of  $1.4 \pm 0.1 \mu\text{m}$ . HR-TEM on the pedant arm of the individual nanostar as displayed in Fig.1d reveals the single crystalline nature. As suggested by SAED, the diffraction pattern suggests that the d-spacing of 0.14, 0.16 and 0.25 nm are attributed to [200], [110] and [101] crystal plane of hexagonal ZnO. The XRD of ZnO nanostars catalyst in Fig.2a exhibits the hexagonal zinc oxide crystal structure with space group P6<sub>3</sub>mc. FTIR spectrum of ZnO nanostars catalysts in Fig.3a shows the stretching of Zn–O in the ZnO nanostars at 428.50 cm<sup>-1</sup>. Furthermore, the bending vibration of H–O–H bonding is located at around 1300 to 1700 cm<sup>-1</sup> respectively [28,29]. For the XPS spectra of ZnO nanostars catalyst (Fig.4), the element of zinc is detected in +2 state with a peak located at 1022.0 eV which is assigned to Zn 2p<sub>3/2</sub> [30,31]. The asymmetric O 1s peak at 530.9 eV is resolved into two distinguishable sub-peaks at 530.9 and 532.1 eV which are ascribed to the lattice oxygen (O<sub>lat</sub>) and surface hydroxyl oxygen (O<sub>-OH</sub>) respectively [30,31]. in which the surface atomic ratio of O<sub>lat</sub>-to-O<sub>-OH</sub> is found to be 1.31.

The as synthesized ZnGly and ZnOI were characterized by SEM, XRD, FTIR and XPS as illustrated in supplementary section. SEM micrographs (Fig. S1) are found to be adopting a nanoplate structure. For the XRD analysis as depicted in Fig. S2, ZnGly exhibits a monoclinic crystal structure of zinc glycerolate with space group P2<sub>1</sub>/c while the XRD pattern for ZnOI matches to standard pattern of zinc oleate. The absorption peaks observed at

512.46 and 650.77  $\text{cm}^{-1}$  in FTIR spectrum of ZnGly (Fig. S3a) are corresponded to stretching of Zn–O. The characteristic alcoholic C–O stretching are presented at 1064.25 and 1124.30  $\text{cm}^{-1}$  while the signal at 1943.14  $\text{cm}^{-1}$  attributes to C–O stretching of hydrogen bonded oxygen (O–H...O) [23,26]. It is obvious from the FTIR spectrum of ZnOI (Fig. S3b) that the  $\text{CH}_2$  rocking of alkyl chain is observed at 722.36 and 744.20  $\text{cm}^{-1}$ . The four intense characteristic peaks at 1398.54, 1465.99, 1526.10 and 1548.63  $\text{cm}^{-1}$  are ascribed to the symmetric and anti-symmetric carboxylate group ( $-\text{COO}^-$ ) [24,32] while the peaks at 2850.87 and 2922.60  $\text{cm}^{-1}$  are ascribed to the symmetric and anti-symmetric stretching of methylene group. The peak at 2944.91  $\text{cm}^{-1}$  is attributed to anti-symmetric stretching of terminal methyl groups. The survey XPS spectrum of the ZnGly as depicted in Fig. S4 reveals that the elements of Zn, O and C exist in ZnGly. The peak at 1022.0 eV can be assigned as Zn 2p<sub>3/2</sub>, which confirms the presence of Zn(II) ion. The asymmetric O 1s peak at 531.9 eV is resolved into two sub-peaks at 531.8 and 532.9 eV which are attributed to alkoxyl oxygen atom and hydroxyl oxygen atom respectively. According to the X-ray crystallographic analysis proposed by Park and co-workers [33], ZnGly adopts a polymeric structure in which zinc atom is surrounded by five oxygen atoms with three glycerolate ligands. The alkoxyl oxygen atoms from glycerolate ligand are responsible to bridge two zinc atoms while hydroxyl group coordinates to one zinc atom and strongly interacts with an alkoxyl oxygen atom through hydrogen bonding. In addition, a symmetric peak at 286.7 eV is certainly attributed to the carbon atom in C–O bond from glycerolate ligand. The survey XPS spectrum of ZnOI in Fig. S4 shows the Zn 2p<sub>3/2</sub> peak at 1022.0 eV. The symmetric peak at 531.9 eV can be ascribed to O 1s in which the oxygen atom is in from of carboxylate ( $-\text{COO}^-$ ). The asymmetric peak at 285.0 eV is attributed to the C 1s region. The peak is resolved into three sub-peaks at 284.7, 285.4 and 288.8 eV which are ascribed to carbon in aliphatic chain (C–C), (C=C) and carboxylate moiety ( $-\text{COO}^-$ ) respectively [34-36]. It is observed that there are no characteristic C 1s signal and O 1s signal for carboxylic moiety ( $-\text{COOH}$ ) which indicates that oleic acid is absent in the ZnOI sample. The proximity of the melting point can also be one of the key identification of the ZnOI. The melting point of synthesized ZnOI is found to be 86 °C which is proximate to 88 °C as reported in literature [37]. Quantitative analysis of Zn in ZnOI by ICP-OES shows that the calculated amount of Zn is less than 1 % deviation from theoretical amount of Zn under the assumption of Zn-to-alkyl chain of oleic acid of 1 : 2. It implies that the ratio of Zn-to-alkyl chain of oleic acid is 1 : 2.

### 3.2. Catalytic performance of Zn catalysts towards the transesterification of refined and unrefined feedstock

As tabulated in Table 3, the ZnO nanostars catalyst showed the catalytic performance ranging from 65.5 % to 99.5 %. An increase of availability of FFA in feedstock sample would generally enhance the catalytic conversion. It is proposed that the ZnGly and ZnOI might be formed during the catalytic reaction due to the availability of FFA and glycerol from transesterification. Furthermore, the ZnGly and ZnOI demonstrated an excellent catalytic performance in transesterification with conversion of 94.6 % and 99.4 %. Additionally, the application of ZnGly and ZnOI as heterogeneous catalyst in transesterification has also been investigated by Reinoso and co-worker [23,24]. In literature, many reports discussed the success of the ZnO catalyzed transesterification of plant oil [19-22,38]. It is an interesting issue to investigate that the main role of ZnO and the fabrication of intermediates and side products during the catalytic reaction.

### 3.3. Study of the ZnO nanostars catalyst in consecutive use towards transesterification

The ZnO nanostars catalyst applied in transesterification of refined canola oil was studied with the results summarized in Table 4 and the catalyst was just reused for at least five cycles without washing steps upon regeneration. The ZnO nanostars catalyst demonstrated a moderate feedstock conversion at 67.9 % in the first catalytic cycle and the feedstock conversion was generally increased to 90.0 % in consecutive use of ZnO nanostar catalyst after the fifth cycle.

Various characterizations were applied in the investigation of the used ZnO nanostars after the fifth cycle of the transesterification. As displayed in SEM micrograph (Fig.1b), the catalyst surface was slightly corroded by both substrates, however, it is still showing its original star-like nanostructure. HR-TEM on the pedant arm of ZnO nanostar exhibits a high crystallinity as depicted in Fig. 1e. The diffraction spots derived from SAED suggests that the d-spacing of 0.25 and 0.28 nm are found and ascribed to [101] and [100] crystal plane of hexagonal phased ZnO while an exceptional diffraction spot with 0.52 nm is found to be [011] crystal plane of monoclinic phased ZnGly. The XRD analysis as illustrated in Fig.2b shows that the diffraction peaks are well-matched with the standard pattern of hexagonal ZnO crystal structure. The FTIR spectrum (Fig. 3b) shows that the absorption band at  $429.85\text{ cm}^{-1}$  is corresponded to the stretching of Zn–O which is similar to the fresh catalyst. XPS analysis as shown in Fig. 4 shows the Zn  $2p_{3/2}$  peak at 1022.0 eV which confirms that the Zn exists in +2 state. The two resolved sub-peaks at 531.1 and 532.3 eV are certainly ascribed to the  $O_{\text{lat}}$  and the  $O_{\text{-OH}}$  respectively. An exceptional increase of the C 1s signal at 285.8 eV assigns to the deposition of ZnGly on the catalyst surface.

In order to certify the *in-situ* formation of ZnGly, a confirmative experiment of the fresh ZnO nanostars catalyst immersed in glycerol at  $140\text{ }^{\circ}\text{C}$  for 15 h was conducted. The immersed ZNO nanostar catalyst was characterized by SEM, XRD, FTIR and XPS (see supplementary section). SEM (Fig. S1c) micrograph shows that there is no observable difference on the surface and the morphological changes. As suggested by SAED micrograph of a single nanostar as illustrated in Fig. S1d, the diffraction ring patterns with d-spacing of 0.25, 0.26 and 0.28 nm are ascribed to [101], [002] and [100] crystal plane of hexagonal ZnO and no perceptible diffraction patterns for ZnGly are observed. The XRD analysis (Fig S2c) shows only the diffraction peak for ZnO and no distinctive XRD pattern for ZnGly is found. The same result is found in FTIR spectrum (Fig. S3c) as it only demonstrates the characteristic stretching of Zn–O at  $426.39\text{ cm}^{-1}$ . XPS analysis as illustrated in Fig. S4 shows that the similar result aligns with the results in TEM, XRD and FTIR with no characteristic ZnGly found.

The confirmative experiment demonstrates that no ZnGly is detected, exhibiting no substantial direct chemical reaction between the fresh ZnO nanostars and glycerol. Zn(II) ions are proposed to be leached out by the trace amount of FFA available in refined canola oil, generating zinc carboxylate salts and finally becoming ZnGly deposited on catalyst surface at the end of the catalysis. The increase of the ZnGly amount on catalyst surface in consecutive transesterification would subsequently increase the catalytic conversion as it is proven to be a promising catalyst [23] to facilitate the transesterification in a faster reaction rate (entry 5, Table 3). As the ZnGly formed in crystalline structure is not significant, it is hard to be detected by XRD and FTIR analysis. In order to prove this proposal, the catalytic transesterification with the presence of higher FFA content was examined.

### 3.4. Study of the ZnO nanostars catalyst in consecutive use towards simultaneous esterification and transesterification

It is found that the rate of the ZnO nanostars catalyzed transesterification depends on the amount of FFA available in the feedstock. As tabulated in Table 3, incomplete conversions of low FFA containing feedstock (entries 1 – 2) and nearly completed conversion of high FFA containing feedstock (entries 3 – 4) were observed.

To find out the threshold FFA content available in feedstock that can significantly facilitate the catalysis, the transesterification was carried out with different addition of oleic acid. As depicted in Fig. 5, the results illustrated that the conversion was generally increased from 0.8 % to 80.6 % with an increase of oleic acid loading from 0.00 wt.% to 6.00 wt.%. With further increased oleic acid loading, the conversion came to level off as it reached the equilibrium. Afterwards, a time domain conversion profile of the simultaneous reaction with threshold oleic acid addition of 6.00 wt.% was performed as illustrated in supplementary section (Fig. S5). The catalytic conversion was achieved in 97.4 % after 2 h. A trace catalytic conversion of 1.3 % was achieved in the background reaction of simultaneous reaction without ZnO nanostars catalyst.

The study of the reusability of ZnO nanostar catalyst in the simultaneous reaction containing 6.00 wt.% of oleic acid was examined with the results as shown in Table 4. The ZnO nanostars catalyst demonstrated faster kinetics with excellent conversion of 97.3 % in the first cycle and maintained at 97 % in consecutive use of catalyst after the fifth cycle.

The morphology, crystal structure and the surface composition of the used ZnO nanostars catalyst was investigated after the fifth cycle of the simultaneous reaction. The SEM (Fig. 1c) micrograph shows that the ZnO nanostars catalyst retains its star-like nanostructure, however, the rough catalyst surface is obviously corroded by substrates. HR-TEM on the pedant arm of individual nanostar as shown in Fig.1f demonstrates a high crystallinity. According to the SAED micrograph, it can be clearly found that the diffraction spots with d-spacing of 0.25 and 0.28 nm are surely corresponded to the [101] and [100] crystal plane of hexagonal ZnO while the diffraction spot of 0.52 nm is found to be [011] crystal plane of monoclinic ZnGly.

The XRD analysis also shows two sets of diffraction pattern as illustrated in Fig. 2c. One of the obvious XRD pattern is certainly matches well with the standard pattern of hexagonal ZnO crystal structure. Another extraordinary diffraction peak is attributed to the monoclinic ZnGly crystal structure which is aligned with the findings in HR-TEM.

The FTIR spectrum corresponding to the used catalyst is quite different from the fresh catalyst as illustrated in Fig. 3c. The absorption band at 420.03 and 651.92  $\text{cm}^{-1}$  are corresponded to the stretching of Zn–O. Apart from this, extraordinary absorption peaks at 1064.69 and 1124.71  $\text{cm}^{-1}$  are attributed to the alcoholic C–O stretching mode while the absorption band at 1944.05  $\text{cm}^{-1}$  is surely attributed to the C–O stretching with the hydrogen bonded oxygen (O–H---O). This characteristic signals supports the existence of ZnGly after five successive simultaneous reactions.

The XPS analysis also confirms that the existence of ZnGly which aligns with results of previous characterization. As shown in Fig. 4, the peak at 1022.0 eV is attributed to the element of zinc which exhibits in +2 state. The two resolved O 1s discernible sub-peaks at 531.3 and 532.6 eV are certainly corresponded to the alkoxy oxygen atom and hydroxyl oxygen atom respectively which indicates the presence of ZnGly on the catalyst surface. The missing O<sub>lat</sub> peak for ZnO is found, probably a thick layer of the ZnGly covered on the catalyst surface. A conspicuous symmetric C 1s peak at 286.4 eV is attributed to C–O in ZnGly.

The reaction intermediate was successfully collected from the reaction mixture and characterized by XRD, FTIR

and XPS which substantiated to be the ZnO. The XRD pattern as depicted in Fig. 2d is well-matched to the standard pattern of ZnO. All the absorption peaks found in FTIR spectrum (Fig. 3d) are similar to the FTIR spectrum of the as synthesized ZnO. Furthermore, XPS analysis (Fig. 4) also demonstrates the same result with the XRD and FTIR analysis.

It is likely that the catalyst surface is corroded by oleic acid in which Zn(II) ion reacts with oleic acid to generate ZnO. The ZnO has been proven to be a promising catalyst to catalyze the reaction with a faster reaction rate. The crystalline ZnGly was found on the catalyst surface and no observable precipitate was collected at the end of simultaneous reaction. It is proposed that the *in-situ* formed ZnO intermediate reacts with glycerol to form crystalline ZnGly which finally deposits on the surface of ZnO nanostar. The special morphology feature of ZnO is beneficial to the electron microscopy characterization as distinct nanoparticles are decorated onto the original nanostar's pedant arm showing a mixed SAED pattern. The ZnO nanostars catalyst does not serve only as the catalyst for biodiesel production but also the source for providing Zn(II) ions and an effective support for the deposition of ZnGly to form a new co-catalyst (Fig. 6), enhancing its catalytic stability and robustness. The similar reaction mechanism for the one-step simultaneous esterification and transesterification, including the initial coordination of methanol and the nucleophilic attack of alkoxide moiety to carbonyl group of triglyceride, has been proposed by Reinoso [39].

ZnO nanostars catalyst is a preferred catalyst and support for this heterogeneous catalytic reaction because of its special morphology. The multi-scaled feature of the ZnO nanostar shows a high surface area to volume ratio as nanoparticles while keeping the overall particle size in the range of micrometer to facilitate more efficient catalyst recovery through centrifugation or filtration. In contrast, pure ZnGly is more difficult to be isolated by centrifugation due to its planar structure and lower density ( $2.2 \text{ g cm}^{-3}$ ) than ZnO ( $5.6 \text{ g cm}^{-3}$ ). According to our studies, ZnO nanostars is found to be a good ZnGly support material as most of the resultant ZnGly were found to be adsorbed on the nanostar with only trace amount of free ZnGly plates found in SEM and TEM observations, it shows that the resultant composite ZnGly/ZnO catalyst would be easier to separated. Furthermore, as both the active ZnO and ZnGly are originated from ZnO, the presence of ZnO nanostar would act as a continuous precursor source for *in-situ* catalyst formation to extend the lifetime of the catalyst. It proves that the ZnO nanostar do tolerate a high FFA contaminant for biodiesel synthesis via one-step simultaneous esterification and transesterification reaction.

#### 4. Conclusion

The multi-scaled ZnO nanostars catalyst was employed as a model catalyst due to its special feature that is beneficial to the characterization of morphological changes by electron microscopy. This catalytic system exhibited a high durability with an increase of reaction rate in successive use of catalyst with a trace amount of ZnGly detected. A proposal of the ZnO intermediate and ZnGly involved in the catalytic conversion has been proven by an experiment of catalytic transesterification with the presence of higher FFA content. The high stability and robustness was observed due to the *in-situ* formation of the ZnO intermediate and the ZnGly deposited on the catalyst surface to form a new co-catalyst. It is confirmed that ZnO nanostars catalyst does not serve only as catalyst towards transesterification but also an efficient support for the deposition of the *in-situ* formed ZnO and ZnGly to enhance the catalyst stability. This paper presented a simple and up-scalable *in-situ* preparation of active ZnGly/ZnO co-catalyst for biodiesel production. The water tolerance of the presented catalyst will be also further investigated on the possibility of applying into low grade feedstock, particularly high water containing feedstock.



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