RASĀYAN *J. Chem.*
Vol. 10 | No. 4 |1323-1329 | October - December | 2017
ISSN: 0974-1496 | e-ISSN: 0976-0083 | CODEN: RJCABP
http://www.rasayanjournal.com
http://www.rasayanjournal.co.in

PREPARATION AND ELECTRO-OPTICAL CHARACTERIZATION OF ZnO THIN FILMS FOR PHOTOCATALYTIC WASTE COOKING OIL TREATMENT

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ABSTRACT

In this study, we have evaluated a new method for treatment of waste cooking oil (WCO) under solar irradiation using zinc oxide (ZnO) thin films. The films were deposited onto a glass substrate by sol-gel thermal spray coating and were characterized by x-ray diffraction (XRD), scanning electron microscopy (SEM) and UV-Vis spectrophotometer. All prepared films showed hexagonal wurtzite structure with a preferred peak at the (002) plane. UV-Vis transmittance spectra indicated that all films had high transparency in visible light region. The optical band gap of thin films decreased from 3.35 eV to 3.22 eV for ZnO and ZnO:Ag, respectively.The quality of the oil was tested using Fourier transform infrared (FTIR) spectroscopy and electro-optical methods. There were significant changes in the characteristic of the WCO after photocatalytic treatment. The peaks at 1733.12–1755.30 cm^{-1} and 2853.81–2921.32 cm^{-1} FTIR data were related to C=O and C–H cluster function, respectively. We obtained the peaks around 1165 cm^{-1} which indicated a characteristic of good commercial oil. From electro-optical measurements, the polarization angle decreased by 1°. From these results, ZnO-based photocatalyst obviously enhanced the quality of WCO. This finding will be useful for treating WCO with a simple and low-cost method.

Keywords: Waste cooking oil, photocatalyst, FTIR, electro-optics.

INTRODUCTION

Indonesia is the biggest palm oil producer in the world. The oil can be further processed to make cooking oil and other products. Used cooking oil cannot be used again because of its toxicity. Many methods have been applied to convert WCO to other useful products, such as detergent, body soap, biodiesel and so on. As far as we know, there is no method to reuse WCO as cooking oil.

Photocatalyst materials have been used for energy and environmental applications. The popular application of photocatalysts in energy is for hydrogen generation from water splitting[1]. In case of environmental applications such as wastewater degradation[2] and anti-bacterial effects[3] have been widely studied. The commonly used photocatalyst materials are titanium dioxide (TiO_2)[4,5], zinc oxide (ZnO)[6-9], tungsten oxide (WO_3)[10], and cerium oxide (CeO_2)[11,12]. Some studies have shown that ZnO is more effective than other photocatalysts.[13] Another application of photocatalysts is the conversion of WCO to biodiesel.[14] However, there is no study of a photocatalytic treatment to reuse WCO.

In this paper, we have evaluated the effect of a ZnO photocatalyst thin film in treating WCO. In previous studies, we found that 7% mol of silver (Ag) in ZnO (ZnO:Ag 7%) thin film showed better photocatalytic activity than pure ZnO, or other doping concentrations.[2,3] Considering this result, we evaluated only pure ZnO and ZnO:Ag 7% thin films. We have characterized the properties of thin films, such as microstructure, morphology and optical properties. WCO samples were analyzed by FTIR and electro-optical methods. Electro-optical methods can be used to investigate the quality of the oil.[15,16]

Rasayan J. Chem., 10(4), 1323-1329(2017)
http://dx.doi.org/10.7324/RJC.2017.1041793

EXPERIMENTAL

The thin films were prepared by a sol-gel thermal spray coating method. The precursor was obtained by mixing zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$ 99.5%, Merck) and isopropanol (IPA) at a concentration of 0.5 M. The mixture was magnetically stirred for 30 min at room temperature. Then, a small amount of mono-ethanolamine (MEA) was added into the solution and was stirred to be a homogeneous solution. In order to prepare ZnO:Ag a 7% solution of $AgNO_3$ was added to a solution of 7 mol% ZnO. The solution was deposited onto a glass substrate at 450 ^oC for 1 h. Prior to deposition, the glass substrates were cleaned using acetone, methanol and deionized (DI) water. The films were characterized by XRD (Shimadzu XRD-7000) from diffraction angle 30^o to 70^o in increments of 0.02^o. The optical properties of the films were analyzed by UV-Vis transmittance spectra. The photocatalytic treatment of WCO was carried out by dipping the films into 25 ml WCO under solar radiation for 2 hours. Finally, WCO samples were analyzed by FTIR and electro-optical methods. The main apparatus for testing the WCO quality was a polariser–analyzer which measured the change of polarisation angle of light after passing through the sample. The schematic diagram of the electro-optical method can be seen in the Fig.-1. In this system, two metal plates with the electric field about 0–10 kV were used to induce the WCO sample. The WCO sample was placed in a cuvette with a diameter about 1 cm. HeNe lamp as a light source with a wavelength of 633 nm was used in this experiment. The temperature of the sample was about 27–28 ^oC with insignificant effect to polarization angle. The polarization change θ was measured for potential difference ϕ from 0 kV to 9 kV with increments of 1 kV for all samples.

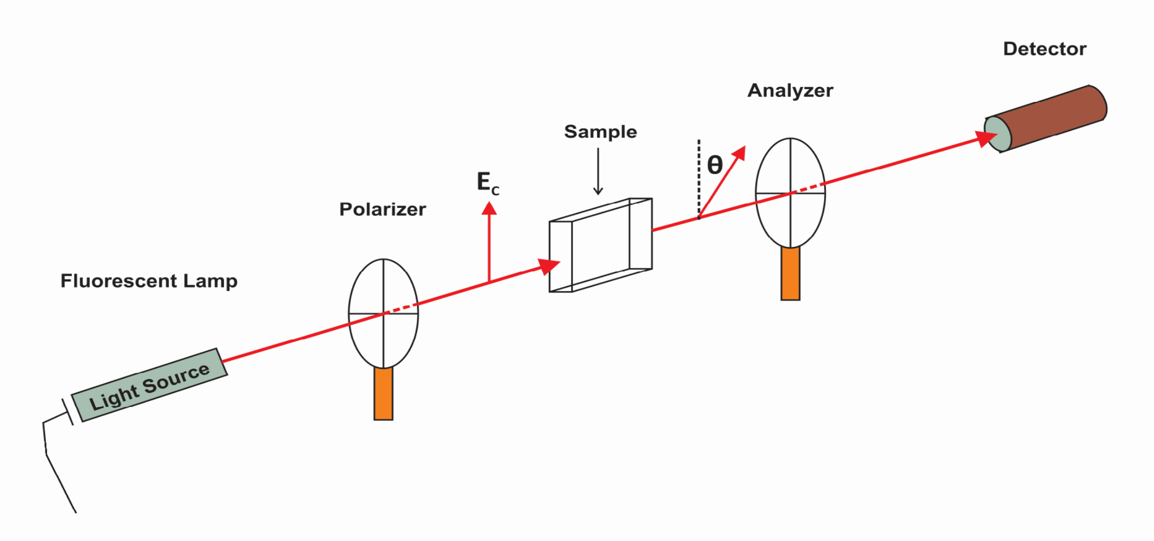


Fig.-1: Experimental setup of the electro-optical method

RESULTS AND DISCUSSION

Crystal Structure

Figure-2 shows XRD pattern of the ZnO and ZnO:Ag thin films. It can be seen that diffraction peaks such as (002), (100), (102) and (103) appeared for all samples. All peaks indicated that ZnO and ZnO:Ag thin films have a hexagonal wurtzite structure, which corresponds to JCDPS data No. #361451. The diffraction peak at the (002) plane showed that FWHM (Full Width at Half Maximum) value of ZnO was 0.17^o and that of ZnO:Ag was 0.37^o. The smaller FWHM value, the better the crystal quality of materials. From this result, the crystal quality of ZnO was reduced by Ag doping. This might be caused by the substitution of Zn atoms by Ag atoms in ZnO lattice which contributed to a reduction in crystal quality.[17]The presence of Ag atoms affected the shift of diffraction peak angle position of ZnO: Ag about 0.02^o, as can be seen in Fig.-2.

The crystallite grain size (*D)* value can be calculated from the (002) diffraction lines of ZnO and ZnO:Ag thin films by the Scherrer formula.[18] The crystallite size of ZnO and ZnO:Ag is about 48.38 nm and 28.55

nm, respectively. We found that the size reduced after Ag doping; this might be caused by substitution of Zn^{2+} ions by Ag^{+} ions.[18]

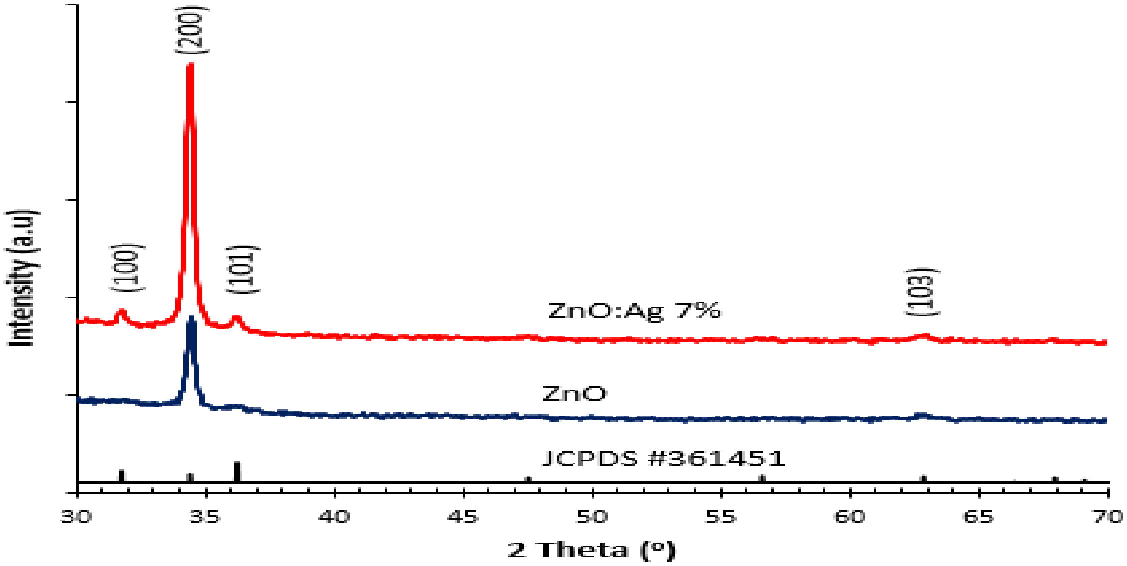


Fig.-2: Thin film XRD-spectra of ZnO and ZnO:Ag.

Lattice strain can be estimated using the Williamson-Hall equation where the relation between the broadening of diffraction peak with crystallite size (*D*) and lattice strain (η) is represented by the following equation:[19]

$$\frac{\beta_{1/2}\cos\theta}{\lambda}=\frac{0.9}{D}+2\eta\left(\frac{2\sin\theta}{\lambda}\right) \tag{1}$$

Where η is lattice strain from the sample.

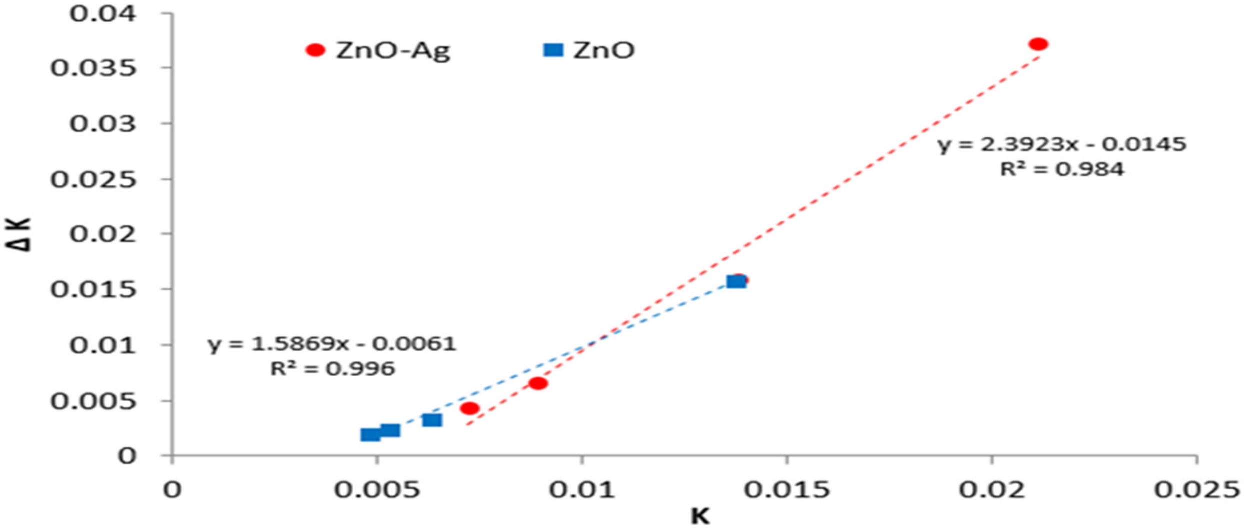
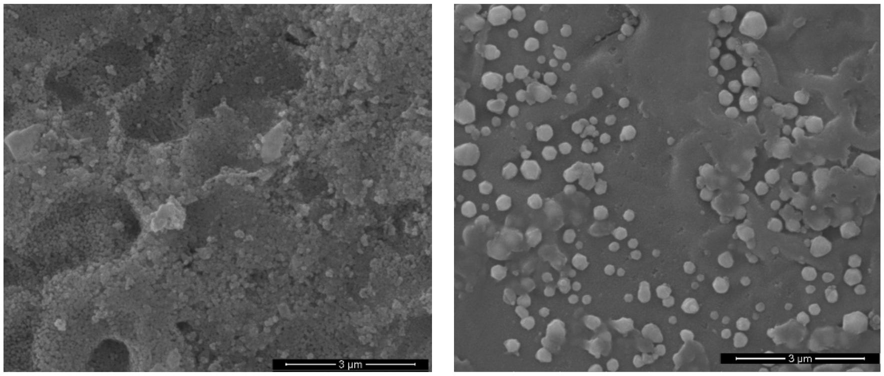


Fig.-3: Classical Williamson–Hall plot of ZnO and ZnO:Ag thin films.

The value of lattice strain is determined by calculating the gradient of line equation which is obtained from line intercept of Williamson-Hall equation graph as shown in Fig.-3. The calculation of this lattice strain result showed that both ZnO and ZnO-Ag have positive strain value (η). It confirmed that the thin films from deposition result had the tensile strain. From the Williamson-Hall equation calculation, we obtained the value of ηZnO = 0.793 and ηZnO-Ag = 1.196.

SEM Analysis

Figure-4 shows surface morphology of ZnO and ZnO:Ag. ZnO thin film has homogenous particle grain distribution with sphere form on its surface. The grain size diameter is about 37.38 – 74.77 nm. The ZnO:Ag surface has heterogeneous particle grain size and the diameter is about 26.32 –67.67 nm. There are a lot of non-uniform particle grains of about 82.71 – 424.80 nm in diameter. These might be caused by substitution of Zn^{2+} ions (radius of 74 pm) by Ag^{+} ions (radius of 115 pm).[20] During deposition, ZnO particles were spread onto a hot glass substrate. The solvent was evaporated before reaching the substrate due to high temperature. It affected the small grain size particles on the substrate as can be seen in the SEM image. This might be caused by oxygen vacancies on the surface of ZnO after Ag replaced Zn atoms.



(a) (b)

Fig.-4: Surface morphology SEM images of ZnO (a) and ZnO:Ag(b) thin films.

Figure-5 shows transmittance spectra of ZnO and ZnO:Ag thin films. The ZnO:Ag film shows a fringe pattern in the visible light region, indicating that the film has a homogenous and good surface,[21,22] while the ZnO film shows a smooth line in the same region. UV-Vis spectra show that the optical absorbance declines in the wavelength range 320–400 nm, demonstrating that the thin films have an optical absorbance in the visible up to UV light region. The optical bandgap can be estimated from the transmission spectra. Prior to calculation, the absorption coefficient should be calculated using the following equation:

$$(\alpha hv)^2 = A(hv - E_g) \tag{2}$$

Where, *hv* is the photon energy, α is the absorption coefficient, A is a constant and *Eg* is the optical band-gap.[23] *Eg* can be obtained by extrapolating the linear part of the curve to $(\alpha hv)^2 = 0$ if one plot $(hv)^2 \sim hv$. The optical band gap of ZnO and ZnO:Ag which are about 3.35 eV and 3.22 eV, respectively. The decrease of band gap energy is related to the conductivity of p-type due to Ag atom impurities. Furthermore, the roughness, porosity of surface and grain boundaries of crystal affected the decreasing band gap energy. The lattice strain exhibited that both ZnO and ZnO:Ag had positive strain values (η). This indicated that the obtained thin films had received tensile strain. From Williamson-Hall equation, the values of ηZnO and ηZnO-Ag are 0.793 and 1.196, respectively. The increase of lattice strain also affected the decrease of the band gap energy.

In order to evaluate the quality of cooking oil, we applied FTIR and electro-optical methods. Figure-6 shows the FTIR spectra of untreated oil and oil treated by photocatalyst. It can be seen that there are changes of the peak in the region of wavelength number 1733.12–1755.30 cm^{-1} and 2853.81–2921.32

cm^{-1}. The two peaks indicate the C=O and C–H bonds for the carbonyl cluster and alkyl cluster, respectively. Both bonds increase after photocatalysis treatment, which may be caused by the reformation of chemical bonds that had been damaged or broken. After photocatalysis treatment, the chemical bonds were formed again. It also can be seen that the peaks around 1165 cm^{-1} increased; these peaks being characteristic of commercial oil.[24] The FTIR results demonstrated that a photocatalytic process can be used for upgrading the quality of WCO.

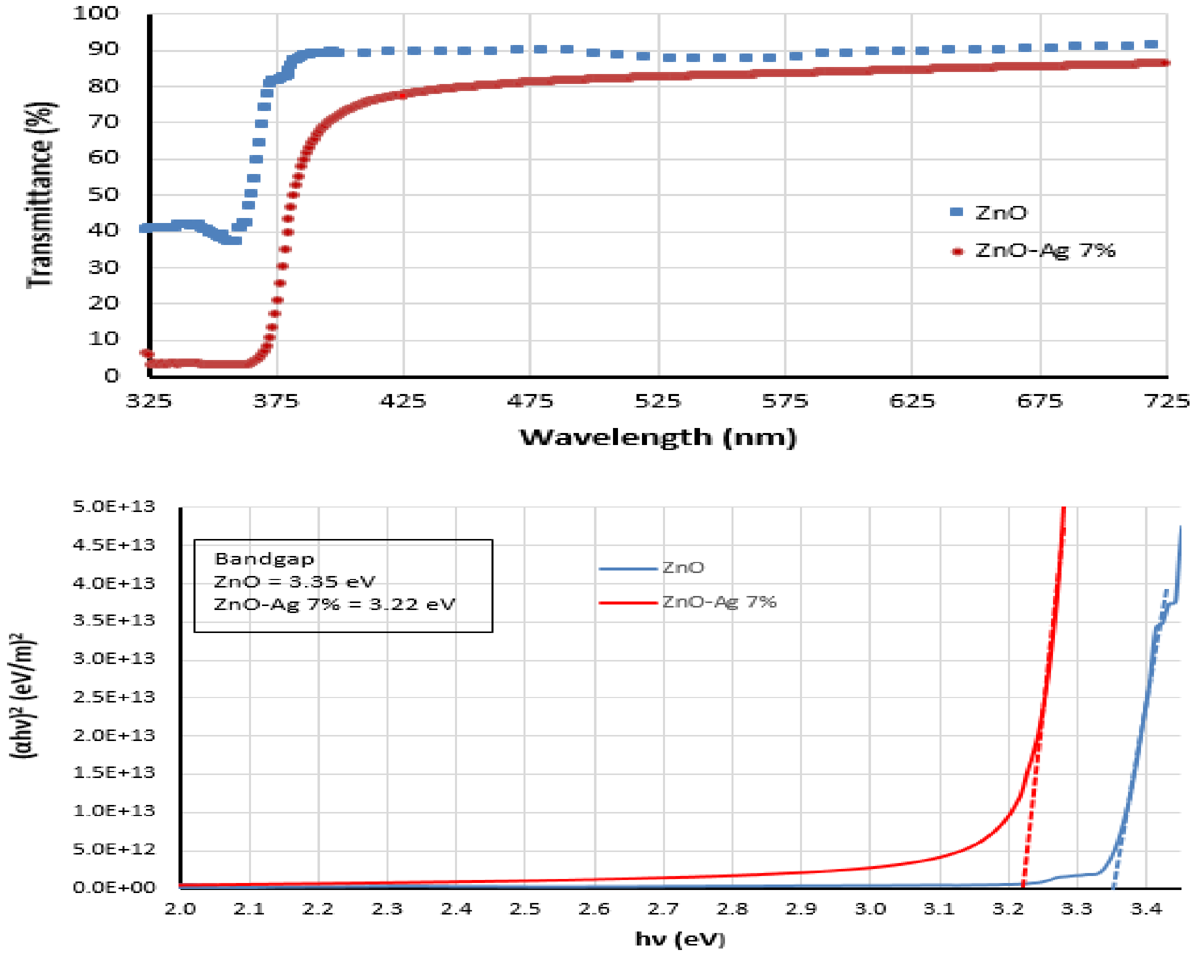


Fig.-5: UV VIS transmittance spectra of ZnO and ZnO:Ag thin films.

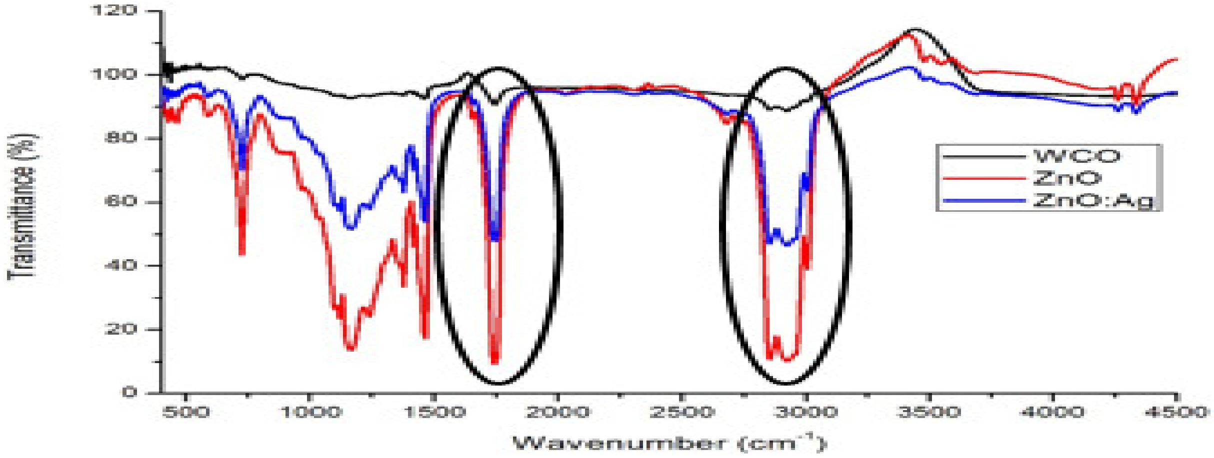


Fig.-6: FTIR spectra of treated and untreated WCO.

The decrease of polarisation angle θ is related to the decrease in the number of free radicals in the oil sample (Fig.-7). This result has been confirmed from GCMS (Gas Chromatograph Mass Spectroscopy). Saturated fatty acids (SFA) played very important role. In previous research, GCMS showed the increase of polarisation angle to be related to the increase of fatty acid components: C17:0 (methyl palmitate cluster, $C_{17}H_{34}O_2$) and C19:1 (methyl oleate cluster, $C_{19}H_{36}O_2$) where both clusters are the components of a triglyceride molecule (TG).[25] In order to explain the increase of polarisation angle of oil, we use two concepts: Van Der Waals interaction and polarizability. Triglyceride molecules (TG) in the oil are known to be non-polar and the pre-dominant interaction in the oil is Van Der Waals force. The interaction Van Der Waals force between one TG molecule and others occurs in the oil. By applying an external electric field, molecule polarisation is increased. The change from a non-polar to a polar molecule increases the Van Der Waals band force and enhances molecule polarisability. A molecule which has high polarisability will produce high polarisation. Van Der Waals band energy, which is related to dissociation energy, will increase up to a certain electric field strength. Above that, the Van Der Waals force will decrease when the TG molecules are far enough apart.

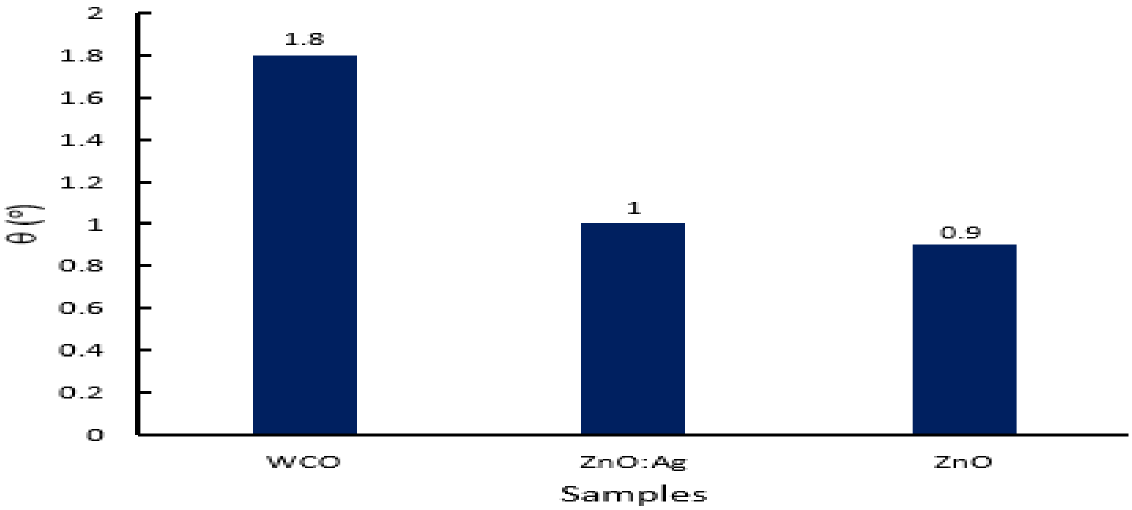


Fig.-7: The change of polarisation angle.

The extreme value of this dissociation energy is called the maximum dissociation energy (ε). The value of $\varepsilon \cong \theta$ where the smaller value of θ, the weaker the Van der Waals interaction and the smaller the TG clusters that can be found in the sample. For this reason, the role of ZnO and ZnO:Ag photocatalyst in oil degradation was to cut the bonds in the C17:0 and C19:1 clusters. This method is simple and economically friendly to evaluate the oil quality. It is also believed that the electro-optical method leads to the finding of a new single parameter of cooking oil quality. It could replace all recent standard parameters of oil quality.[16] In our result, low polarisation angles were obtained after photocatalysis treatment indicating the good quality of the cooking oil. The best explanation of the WCO becoming of good quality lies in the photocatalytic treatment that breaks the long-chain saturated fatty acids and increases the shorter fatty acids. In Fig.-7, it can be seen that the lowest polarisation angle occurred after treatment using ZnO thin film. This may be because the Ag substitution in ZnO reduced the crystal quality and did not work so effectively to upgrade the WCO quality.

CONCLUSION

ZnO and ZnO:Ag thin films have been prepared for photocatalytic treatment of WCO. The addition of Ag into ZnO materials reduced the crystal quality. From transmittance spectra, it can be seen that the films have high transparency in the visible light region. The optical band gap of the thin film decreased slightly from 3.35 eV to 3.22 eV for ZnO and ZnO:Ag, respectively. FTIR showed that there was the formation of C=O and C–H bonds. The increase of peaks around 1165 cm^{-1} indicated the peaks of commercial oil. The electro-optics of WCO showed a decrease of polarisation angle of below 1^{o}.

ACKNOWLEDGEMENT

The authors would like to thank Ministry of Research, Technology and Higher Education of the Republic of Indonesia for funding this research in 2017.

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[RJC-1793/2017]