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Research paper



Synthesis and Physiochemical Properties of Zinc Layered Hydroxide-Cinnamate

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Abstract

The intercalations of cinnamic acid into zinc layered hydroxide were synthesized by using simple direct method due to the less usage used and simple preparation steps. The physiochemical studies were done to determine the ability of zinc layered hydroxide to traps cinnamic acid in between its interlayer region. The FTIR shows new generation of peak such as OH group, C=O, C=C, C-O and trans C=C at 3379 cm^{-1}, 1643 cm^{-1}, 1578cm^{-1},1253 cm^{-1} and 873 cm^{-1}, and increases in basal spacing at 22.06Å indicate the intercalations of cinnamic acid into the zinc layered hydroxide were presence. The morphological surfaces show new changes toward the surfaces of the intercalated compounds.

Keywords: *cinnamic acid; cinnamate; intercalation; layered hydroxide salts; zinc layered hydroxide*

1. Introduction

Sun radiation are known to help improving the production of vitamin D body that help in increasing the calcium absorption, blood-pressure regulation and even emotional psychological effects [1]. However, due to thinning of ozone layer causes high intensity sun radiation penetration towards the earth surfaces deteriorate human health. Thus, the usage and production of sunscreen has been widening, not only used during picnic and sports but also in cosmetics production.

Cinnamic acid (CA) is a type of organic UV filters that able to absorb photon and able to return to ground state by emitting energy thermally through series of vibrational transitions [2], and lose its functionality if photodegradation process take placed. Besides that, these organic sunscreen have been reported to cause allergic contact dermatitis and sometime not able to absorb wide range of sun radiation [3].

Layered Hydroxide salts (LHS) is one of the layered compound that have the hydroxide layer composed of metal cations with one valancy and the positive charges are develop form under-coordination or mixed geometrics of intralayer cations [4]. The general formula of zinc layered hydroxide (ZLH) is $M^{2+}(OH)_2$-x(An-)x/n.yH_2O, where M^{2+} is the metallic cation and An^- is the exchangeable ion or counter ion [5] that able to balance with the layered structure which then gives out total of neutral charges. ZLH are known to have a brucite like layers with one quarter of octahedrally coordinated zinc atoms replaced by tetrahedrally coordinated zinc atoms located below and above the plane [4]. According to [6], intercalating organic anions into the layered structured provide great advantages such as

i) sunscreen stabilization because the interlayer region of the layered compound were considered as the microvessel that able to store anionic molecule,
ii) wide range absorption of the ultraviolet radiation, and
iii) acts as the protection barrier between the skin and the filter which can reduce or even eliminate the allergy problems

The intercalation and physiochemical properties of cinnamic acid (CA) into the zinc layered hydroxide (ZLH) were investigated in this paper.

2. Methodology

2.1. Materials

99% Zinc oxide (ZnO), R&M; 99 % trans-cinnamic acid (CA), Sigma Aldrich; 99% Sodium hydroxide (NaOH), R&M. All other chemicals were analytical prepared.

2.2. Synthesis of zinc layered hydroxide-cinnamate

The synthesis of Zn/Al-LDH-CA was prepared by using simple direct method. The prupose of using this method due to the simple synthesis method with few chemical, less preparation steps and non-usage of complex instruments [7]. First, 0.2g of ZnO was mixed thoroughly by using 90% methanol and 10% water. Then, addition of cinnamate ion was added gradually. The pH was adjusted to pH 7± 0.5 using dropwise of 2M sodium hydroxide (NaOH). The solution mixture was stirred for 5 hours for the intercalation process to happen thoroughly. The obtained mixture undergoes aging process for 18 hours in 70˚C oil bath shaker. The slurry that obtained were and centrifuge and washed for 3 times by using deionized water to ensure the excess impurities were completely removed before drying in 70˚C oven. The sample then was kept for characterization purposes.

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2.3. Characterizations of Zn/Al-LDH-CA

The Fourier Transform Infrared -Attenuated Total Reflectance (FTIR-ATR) spectra were obtained from FTIR Thermo-USA, to determine the functional group present in the sample. The Powder X-Ray Diffraction (PXRD) pattern were obtained by using Rigaku Mini-2 using CuKα), to understand basal spacing value. Field emission Scanning Electron Microscopic (FESEM) images were obtained by using Carl Zeiss SUPRA 40VP.

3. Results and Discussions

3.1. Fourier transforms infrared-attenuated total reflectance spectroscopy (FTIR-ATR)

Figure 1 and Table 1 show synchronization between the value and FTIR-ATR spectra of the ZnO, CA and 0.35M ZLH-CA. For ZnO spectra, we could observe the presence of M-O vibration which are at the lower IR region, 454 cm-1 and 560 cm-1. Pure ZnO are known to have weak absorption band in regions from 560 cm-1 to 550 cm-1 and from 520 cm-1 to 500 cm-1 and a very significant strong centered band around 450 cm-1 [8]. Meanwhile for CA FTIR peak, we could observe the presence of C=O group, C=C group, C-O group and Trans C=C group at 1676 cm^{-1}, 1629 cm^{-1}, 1285 cm^{-1} and 945 cm^{-1}.

FTIR spectra for 0.35M were observed to shift slightly towards the lower region. According to the [9], some peaks are slightly shifted to the lower region due to the interactions between the organic anions and the host layers. The presence of OH group, C=O, C=C, C-O and trans C=C at 3379 cm^{-1}, 1643 cm^{-1}, 1578 cm^{-1},1253 cm^{-1} and 873 cm^{-1}. According to [10], the band observed in lower region (<600 cm-1) can be deduce as the lattice vibration mode such as M-O-H vibration and O-M-O stretching. The presence of this functional group which previously can be observed from the FTIR spectra of (CA) concluded that the intercalation of CA were successful in between the ZLH interlayer regions.

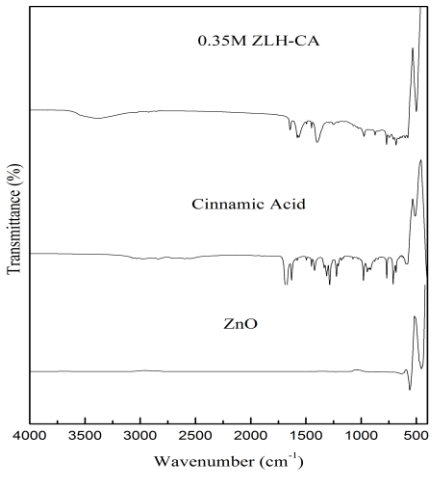


Fig. 1: FTIR spectra for ZnO, Cinnamic acid (CA) and 0.35M ZLH-CA

Table 1: FTIR-ATR vibrational wavenumber for ZnO, Ca and 0.35M ZLH-CA.

Sample	Functional Group	Wavenumber (cm^{-1})
ZnO	M-O	454, 560
Cinnamic acid (CA)	C=O	1676
	C=C	1629
	C-O	1285
	Trans-C=C	945
0.35M ZLH-CA	OH	3379
	C=O	1643
	C=C	1578/1565
	C-O	1253
	Trans C=C	873.

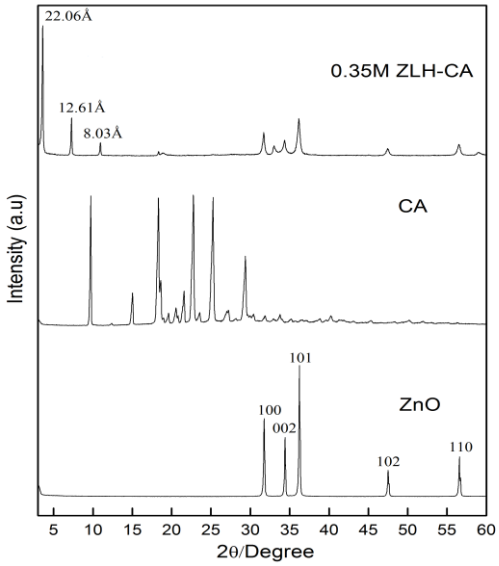


Fig. 2: PXRD pattern for ZnO, CA and 0.35M ZLH-CA

3.2. Powder X-ray diffraction analysis (PXRD) and surface morphology.

The PXRD pattern as shown in Figure 2 indicates the characteristics before and after intercalation process takes placed. The PXRD pattern of the intercalated compounds shows that the compound are crystalline type compound due to the well-defined, narrow, sharp and significant peak [11]. For ZnO PXRD pattern, the 5 fingerprints peaks of ZnO were observed in between 30˚ to 60˚, with lattice plane of 100, 002, 101,102 and 110 that shows high crystallinity of the ZnO precursors [7]. Meanwhile, the 0.35M of ZLH-CA shows increase in basal spacing to the lower region. The new basal spacing at 22.06Å and formation of three harmonic peaks indicates the availability of CA intercalated in between the ZLH interlayers. The expansion happen due to the spatial orientation as well as the molecular size of the organic anions intercalated in between the interlayer regions. However, the intercalation of 0.35M ZLH-CA were slightly incomplete due to the presence of ZnO traces in between the 2θ = 30˚ - 60˚.

The process of inserting CA in to interlayer region of ZLH is known to undergoes three step through dissociation-deposition mechanism [12,13]. The first step involves the hydrolysis of ZnO in water. When ZnO being introduced into the water, the surface of the ZnO are being hydrolyses to form $Zn(OH)_2$ (Eq 1). Then, formation of $Zn(OH)_2$ layer are becoming more soluble with the presence of acid compared the previous precursor ZnO, to form Zn^{2+} and OH^- (Eq 2). The organic anions, cinnamate (CA^-), Zn^{2+} species and water presence inside the solution are reacted together to form layered intercalation compound (Eq 3).

$$ZnO + H_2O \longrightarrow Zn(OH)_2 \quad (1)$$

$$Zn(OH)_2 \longrightarrow Zn^{2+} + 2OH- \quad (2)$$

$$Zn^{2+} + 2OH^- + CA^- \longrightarrow Zn^{2+}(OH)_{2-x}(CA^-)_x.nH_2O \quad (3)$$

Based on the average basal spacing of the intercalated compound which is 22.06Å, the calculated gallery height is 11.66Å, by subtracting the thickness of the brucite layer (4.8Å) and every zinc

tetrahedron (2.6Å). Based on the calculated value of the gallery height, the CA were oriented in monolayer manner. The illustration on the three dimensions of the molecular structure of CA and spatial orientation of CA intercalated in between the layers of the ZLH was shown in Fig 3. The surface morphology for ZLH-CA and ZnO were shown in Fig 4. ZnO has a no uniform granular structure without any specific shape as mention by [7]. Meanwhile, after the intercalation of the Ca into the ZLH interlayer regions, the morphology images show the needle thread-like structures with no uniform shape. The summarization of the finding with others researchers were tabulated in Table 2.

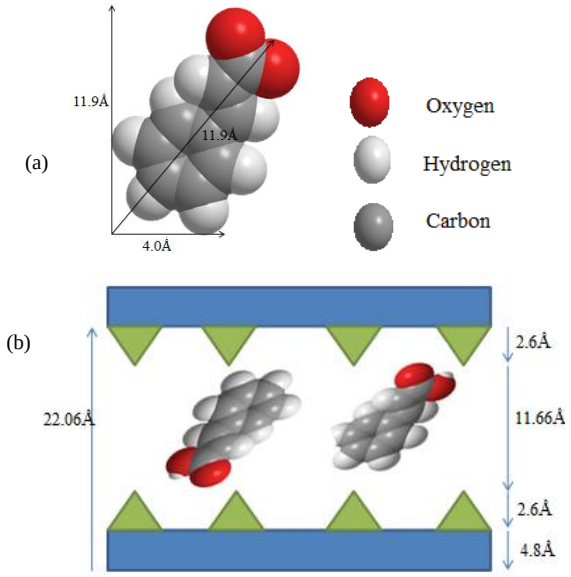


Fig. 3: Illustration on the molecular model of CA (a) and spatial orientation of CA in between the ZLH interlayer region.

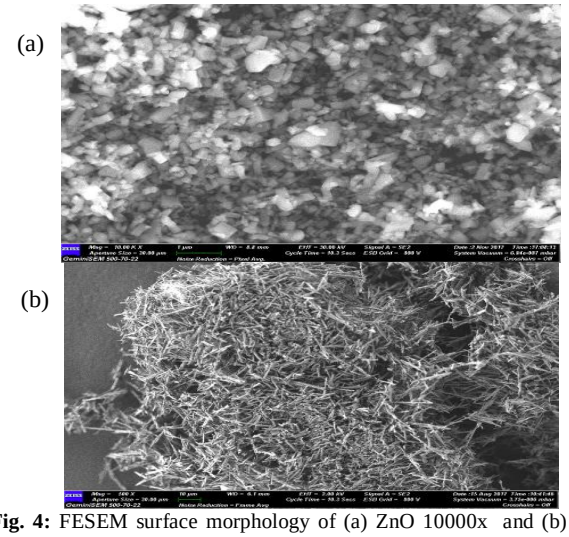


Fig. 4: FESEM surface morphology of (a) ZnO 10000x and (b) 0.35M ZLH-CA at 500x.

Table 2: Summarization on the finding results with other researcher.

	Findings	Other researchers	References
FTIR			
ZnO	454cm^{-1}, 560 cm^{-1}	560 cm^{-1} -550 cm^{-1} or 520 cm^{-1} - 500 cm^{-1} Strong centered band at 450 cm^{-1}	Machovaky et. al (2013)
PXRD			
ZnO	2θ = 30˚ - 60˚	30˚ - 60˚, with lattice plane of 100, 002,101,102 and 110	Ahmad et. al (2016)

4. Conclusion

The intercalations of CA into the interlayer regions were successful by the interpretation of the PXRD pattern that shows the increase of basal spacing of the crystalline compound at 22.06Å. The , FTIR spectra show the presence of the functional group of CA after the intercalation process has taken placed such as OH group, C=O, C=C, C-O and trans C=C at 3379 cm-1, 1643 cm-1, 1578cm-1,1253 cm-1 and 873 cm-1 FESEM show the changes of the morphological surfaces in pure ZnO and intercalated compound.
In following work, we will investigated the effect of solvent, pH and the stirring effect toward the intercalation process of the cinnamic acid into the interlayer region of the ZLH.

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