MICROSTRUCTURAL AND OPTICAL PROPERTIES OF NANO-SIZED ZNO/ZNAL₂O₄ MIXED METAL OXIDES PREPARED BY THERMAL TREATMENT APPROACH

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Abstract— This article reports the synthesis of Zn/ZnAl₂O₄ as a thin film-based Zn/Al-NO₃ layered double hydroxide (Zn/Al-LDH) through combination of thermal treatment and co-precipitation methods. The prepared thin film of Zn/Al-LDH underwent calcination in furnace with 450 oC to obtain the Zn/ZnAl₂O₄ thin film in mixed metal oxides (MMO) form and remove organic compounds. The structural studies of both Zn/Al-LDH and Zn/ZnAl₂O₄ thin films have been carried out using XRD. The XRD spectra showed that the formation of crystalline structure of the prepared samples. The optical properties were investigated using a UV–Vis spectrophotometer and luminescence spectrometer, which showed band gap of 3.2. These results prove that, the modified coprecipitation and thermal treatment methods are simple and cost-effective techniques that can produce quite pure MMO thin film with no additional processes or chemicals needed.

Keywords— Mixed Metal Oxides, Layered Double Hydroxide, Zn/ZnAl₂O₄

1. INTRODUCTION

Layered double hydroxides (LDHs) show an enormous number of applications as catalyst, drug delivery, photo-response and micro container, etc [1-3]. Thermal treatment of LDHs is stated as a substitute approach to the traditional physical and chemical procedures for the preparation of mixed metal oxide (MMO). A breakdown of the 2D LDH layered structure was caused by the thermal treatment of the LDH after that a formation of MMO composed of metal oxide and spinal phase with large surface area. In lithium ion batteries, a great interest is shown by MMO due to its quite large surface area. In the solar energy conversion, MMO has garnered a huge potential especially in photocatalyst [2, 4-6]. The MMO offers large potential in manufacturing on a wide scale due to its good quality control, low cost and high purity [7-9]. Earlier, few studies regarding LDH producing, its optical and its electrical properties were found. However, thermal treatment effect on these properties as a function of the molar ratio were not studied [9, 10]. In this attempt, a chain of Zn/Al-LDH have been manufactured by coprecipitation method at number for Zn⁺² to Al⁺³ molar ratio of 3, 4, 5 and 6 using a pH value of 7.5. In addition, a thermal treatment was made for the prepared samples at 450

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°C to change them to ZnO/ZnAl₂O₄ thin film (MMOs). Structural, thermal and optical were also investigated in detail.

2. METHODOLOGY

Fluorine dop ed Tin Oxide (FTO) (2.2 mm, 15 ohm) was purchased via Solaronix. FTO glasses were washed thoroughly using sonication by soppo water, DI water, ethanol and acetone. While other materials involving NaOH (99%), Zn (NO₃)₂ · 6H₂O (98.1%), and Al (NO₃)₃ · 9H₂O (98%), were bought by Sigma (St Louis, MO). Zn/Al-NO₃-LDH preparation was carried out using coprecipitation method described [11]. A 2 mol/L NaOH in hydrous solution was blended with 250 mL of solution comprising Al³⁺ and Zn²⁺. PH of 7.5 was acquired in this experiment via drop addition of NaOH; the obtained solution was in the form of a white residual. The solution of white residual form was washed and centrifuged with ethanol thoroughly and dried using an oven at 60 °C. The obtained powder was mixed with Polyethylene Glycol (PEG) and few drops of ethanol and left to stir for 6 hours. The final product was deposited on FTO substrate by Dr Blade method. Then the thin films were calcined at 400 °C with different molar ratio to form the MMO structure.

3. RESULTS AND DISCUSSION

Figure 1 shows the TGA-DTG curves of Zn/Al-NO₃-LDH at molar ratio 4:1 of Zn to Al. Three stages of degradation can be seen from the general behavior of LDH TGA curve. Below 180 °C which is due to the release of water from the surface and the LDH interlayer. The second stage in the range of 180–300 °C which is because of the brucite-like layers dehydration. The last stage is attributed to the decomposition of the nitrate ions in the interlayer between 300 to 500 °C. Figure 1 also shows the DTG curve. The DTG curve illustrates three main peaks. The first one which is around 121 °C is attributed the water removal from the Zn₄Al-LDH structure. In the meanwhile, peaks at 238 and 315 °C of Zn₄Al-LDH are corresponded to the nitrate ions decomposition in the interlayer of Zn₄Al-LDH.

Fig. 1 TGA and DTG curves of Zn₄Al-NO₃-LDH at heating rate of 10 °C/min

Figure 2 shows the XRD patterns of the prepared LDHs thin films ($\text{Zn}_3\text{Al-NO}_3$, $\text{Zn}_4\text{Al-NO}_3$, $\text{Zn}_5\text{Al-NO}_3$ and $\text{Zn}_6\text{Al-NO}_3$). The XRD diffraction patterns was used to identify the LDH structure. The basal and higher-order reflection at 9.8° , 19.8° , 29.8° and 60.25° were found at LDH diffraction peaks of 003, 006, 009 and 110, respectively. The values of basal spacing for (d003), (d006), (d009) and (d110) were found to be 8.95, 4.47, 2.65 and $1.53 \text{ \AA}$, respectively. These values were gotten from the XRD software, which in a good agreement with the literature [12].

Fig. 2 PXRD patterns of $\text{Zn}_r\text{Al-LDH}$; where r is 3, 4, 5 and 6

A breakdown of the 2D LDH layered structure was occurred due to the thermal effect on the LDH followed by a formation of MMO composed of metal oxide and spinal phase. Figure 3 shows XRD patterns of the calcined LDH (MMO) thin films. A reduction in the molar ratio of $\text{ZnO}/\text{ZnAl}_2\text{O}_4$ resulted in an improvement in the sharpness and the intensity of the (440) reflection ($2\theta = 66.69$ degrees) which indicates the increase of the ZnAl_2O_4 spinal phase in the final nanocomposite. The results suggest that reflections belong to ZnAl_2O_4 spinal phase started to be observed at low molar ratio. In the $\text{Zn}_3\text{Al-MMO}$ and $\text{Zn}_4\text{Al-MMO}$ samples, orientations of the (400) and (511) reflections were obtained and started to disappear with the increased of the molar ratios ($\text{Zn}_5\text{Al-MMO}$ and $\text{Zn}_6\text{Al-MMO}$).

Fig. 3 PXRD patterns of (a) $\text{Zn}_r\text{Al-MMO}$; where r is 3, 4, 5 and 6

4. CONCLUSION

The modified co-precipitation and thermal treatment methods are proved to be simple, cost effective, and uncomplicated apparatus methods to fabricate a thin film of Zn/Al-MMO with high purity and Environmentally friendly because of low toxic free by-product and the lack of chemical reagents used.

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