UNIVERSITI PUTRA MALAYSIA

SYNTHESIS AND CHARACTERIZATION OF ZINC-ALUMINIUM LAYERED DOUBLE HYDROXIDE NANOCOMPOSITE PREPARED VIA COPRECIPITATION METHOD

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By

ABDULLAH AHMED ALI AHMED

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Doctor of Philosophy

September 2012

DEDICATION

To my wife

with gratitude and love

I dedicate this work

Abstract of the thesis presented to the senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Doctor of Philosophy

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Chairman: Zainal Abidin Talib, PhD

Faculty: Science

Zinc–Aluminium Layered Double Hydroxides (Zn–Al–NO_3–LDHs) were prepared using the coprecipitation method at different Zn^{2+}/Al^{3+} molar ratios (2, 3, 4, 5 and 6) with adjusting pH value at 7.5 and at different pH values (6, 7, 8, 9 and 10) with constant molar ratio of 4. The second part of the work is the calcination of Zn–Al–NO_3–LDH sample prepared at Zn^{2+}/Al^{3+} molar ratio of 4 and pH value of 7 at two temperature ranges; 50–500 °C and 200–1000 °C. The structural, textural, morphological, thermal and optical properties were studied for all the samples. In addition, the dielectric responses and ESR spectra were also investigated.

Analysis of the XRD spectra of LDH showed that the crystallite size was in the range of 15–36 nm which confirmed that the LDH is a nanocomposite. This is corroborated by the results of unit cell parameters (*a* and *c*) which showed that the construction of LDH resulted in nanolayers. For the calcined LDH sample at 200 °C and above, the crystallite size were in the range of 42.7–51.2 nm which is attributed to the formation nanostructure of ZnO phase.

For the samples prepared at different Zn^{2+}/Al^{3+} molar ratios, the crystallinity of LDHs was found to improve as molar ratio decreased due to the distortion of the hydroxide sheet networks of the LDH crystal by the larger difference in ionic radii of Zn^{2+} and Al^{3+}. On the other hand, the crystallinity of the samples prepared at different pH-values was improved as the pH-value increased due to the increasing of the precipitation of Zn^{2+} ions into the LDH slurry. For the calcination temperature below 200 °C, LDH structure was well preserved, but started to collapse and transformed to zinc oxide (ZnO) phase at 200 °C and above, due to the water loss and decomposition of nitrate anions of LDH interlayer. At 600 °C and above, $ZnAl_2O_4$ spinel was formed and the crystallinity of ZnO and $ZnAl_2O_4$ improved as the calcination temperature increased.

Optical band gap of the samples was calculated using Kubelka-Munk model. The band gaps arise due to the electronic direct transitions in the brucite-like layers and nitrate anions (NO_3^-). Band gaps were affected by the molar ratios used due to the formation of low crystalline phases (ZnO and $ZnAl_2O_4$). This affect was also observed by the variation of pH-value. Band gap decreased as the calcination temperature increased

within the experimental temperature range of 200–1000 °C. The decreased in band gap value was related to the improvement of the photocatalytic activity due to the increased of the ZnO crystal size.

The dielectric response of the LDH is believed to be caused by two charge carriers: the protons of the LDH water molecules and the NO_3^- interlayer anions, which can be described by the anomalous low frequency dispersion with the second type of Universal Power Law. The dominance of ZnO dipoles and charge carriers (NO_3^- ions) in the dielectric relaxation increases with the increasing molar ratio. The dielectric response for the LDH calcined above 150 °C is similar to the dielectric response of ZnO, because of the presence of the ZnO phase in the LDH at this temperature range.

The *in situ* electron spin resonance (ESR) spectra of fresh LDH obtained at room temperature up to 190 °C were studied. These spectra were due to the presence of nitrate anions in the LDH interlayer. However, at calcination temperature of 200 °C and above, ESR spectra (*ex situ* ESR spectra) were due to the oxygen vacancies of ZnO which was formed during thermal treatment of LDH. At 600 °C and above, there is an interaction between the oxygen vacancies of $ZnAl_2O_4$ and the aluminium atom. The overlapped signal can be resolved into two signals from the $ZnAl_2O_4$ spinel and the ZnO phase at 1000 °C.

Thermal diffusivity of LDH as a function of *in situ* temperatures result in a nonlinear relation which is due to the changing of water content of LDH when the temperature was

increased. However, thermal diffusivity of LDH as a function of calcined temperatures showed a linear relation and the slope of these data demonstrated the dependency between thermal diffusivity and water content of LDH below 200 °C. For temperatures above 180 °C, the thermal diffusivity behavior was mainly governed by ZnO phase in the LDH. Thermal diffusivity of LDH as a function of molar ratio also resulted in a nonlinear relation which is due to the formation other phases namely ZnO and $ZnAl_2O_4$ with LDH, when the molar ratio was decreased or pH-value was increased.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

SINTESIS DAN PENCIRIAN TERHADAP SEBATIAN NANOKOMPOSIT ZINK-ALUMINIUM LAPISAN BERGANDA HIROKSIDA DISEDIAKAN MELALUI KAEDAH SEPEMENDAKAN

Oleh

ABDULLAH AHMED ALI AHMED

September 2012

Pengerusi: Zainal Abidin Talib, PhD

Fakulti: Sains

Penyediaan zink-aluminium hiroksida berlapis ganda menggunakan kaedah ko-pemendakan pada kadar Zn^{2+}/Al^{3+} yang berbeza nisbah molar (2, 3, 4, 5 dan 6) dan pada nilai pH 7.5, dan pada Kedua nilai pH yang berbeza (6, 7, 8, 9 dan 10) dengan menetapkan nisbah molar Zn^{2+}/Al^{3+} pada 4. Bahagian kedua kajian ialah penyediaan sampel yang terkalsin Zn-Al-NO_3-LDH pada nisbah molar 4 dan nilai pH 7 dandua julat suhu. 50–500 °C dan 200–1000 °C. Kajian berkenaan struktur, tekstur, sifat morfologi, terma dan optik dilakukan ke atas semua sampel. Analiis berkenaan respons dielektrik dan spektrum ESR juga telah dilakukan.

Analisis spektrum XRD LDH menunjukkan bahawa saiz crystallite adalah dalam julat 15-36 nm yang mengesahkan bahawa LDH adalah komposit nano. Ini disokong oleh keputusan parameter sel unit (*a* dan *c*) yang menunjukkan bahawa pembinaan LDH mengakibatkan lapisan nano. Bagi sampel LDH dikalsin pada suhu 200 °C dan ke atas, saiz crystallite adalah dalam julat 42.7-51.2 nm yang dikaitkan dengan pembentukan struktur nano ZnO fasa.

Analisis Spektrum XRD LDH menunjukkan bahawa saiz crystallite adalah dalam julat 15-36 nm yang mengesahkan bahawa LDH adalah Komposit nano. Ini disokong oleh keputusan parameter sel unit (*a* dan *c*) yang menunjukkan bahawa pembinaan LDH mengakibatkan nanolayers. Bagi sampel LDH calcined pada suhu 200 ° C dan ke atas, saiz crystallite adalah dalam julat 42.7-51.2 nm yang dikaitkan dengan nanostructure pembentukan ZnO fasa.

Sampel Zn^{2+}/Al^{3+} yang disediakan dengan berbeza nisbah molar menunjukkan kehabluran LDH meningkat apabila nisbah molar menurun. Perbezaan yang ketara antara jejari ion Zn^{2+} dan Al^{3+} menyebabkan pengherotan kristal rangkaian lapisan hiroksida kristal LDH. Kehabluran juga didapati meningkat apabila nilai pH meningkat. Ia disebabkan oleh pemendakan ion Zn^{2+} meningkat dalam sluri struktur LDH tidak terjejas apabila pengkalsinan di lakukan di bawah suhu 200 °C. Tetapi, ia mula mengalami keruntuhan dan berubah menjadi zink oksida pada suhu 200 °C dan ke atas Ia di sebabkan oleh kehilangan air dan penguraian anion nitrat pada lapisan LDH.

$ZnAl_2O_4$ spinel terbentuk pada suhu 600 °C dan ke atas, dan kehabluran ZnO dan $ZnAl_2O_4$ meningkat apabila suhu pengkalsinan meningkat.

Model Kubelka-Munk digunakan untuk mengira celah jalur tenaga setiap sampel celah jalur tenaga meningkat disebabkan peralihan elektronik langsung dalam lapisan bersifat *brucite* dan anion nitrat (NO_3). Perubahan nisbah molar mempengaruhi nilai celah jalur tenaga. Ia disebabkan oleh pembentukan fasa ZnO dan $ZnAl_2O_4$ yang kehablurannya rendah. Kesan yang sama juga dapat dilihat pada pelbagai nilai pH. Experimen yang di jalankan dalam julat suhu 200-1000 °C menunjukkan nilai celah jalur tenaga berkurangan apabila suhu pengkalsinan meningkat. Pengurangan nilai celah jalur tenaga berkait dengan peningkatan aktiviti fotopemangkin yang di sebabkan oleh peningkatan saiz hablur ZnO.

Respons dielektrik LDH dipercayai disebabkan oleh dua pembawa cas: iaitu proton dari molekul air LDH dan lapisan anion, NO_3^-. Fenomena ini dapat dijelaskan kerana penyebaran frekuensi rendah yang abnormal (ALFD) berkaitan dengan Hukum Kuasa Universal ke kedua. Dominan ZnO dwikutub dan pembawa cas (NO_3^- ion) dalam pengenduran dielektrik meningkat apabila nisbah molar meningkat. Pengkalsinan LDH pada suhu lebih dari 150°C menunjukkan respons dielektrik yang sama dengan respons dielektrik ZnO yang disebabkan oleh kehadiran fasa ZnO dalam LDH pada julat suhu tersebut.

Elektron putaran resonans *in situ* (ESR) spectrum dari suhu bilik hingga 190 °C dijalankan keatas sampel LDH yang baharu (tanpa apa-apa rawatan) . Spektrum yang diperolehi di sebabkan oleh kehadiran ion nitrat dalam lapisan LDH. Tetapi, pada suhu pengkalsinan 200 °C dan ke atas, ESR spektrum (*ex situ* ESR spektrum) di sebabkan oleh kekurangan oksigen dalam ZnO yang terhasil ketika rawatan haba ke atas LDH dilakukan. Pada suhu 600 °C dan ke atas, saling tindak balas berlaku antara kekurangan oxigen dalam $ZnAl_2O_4$ dan nukleus aluminium. Isyarat bertindih yang terhasil dapat di selesaikan menjadi dua isyarat berasingan oleh $ZnAl_2O_4$ spinel dan fasa ZnO pada suhu 1000 °C.

Peresapan haba LDH sebagai fungsi terhadap suhu *in situ* menghasilkan hubungan tidak linear. Ia disebabkan oleh perubahan kandungan air dalam LDH apabila suhu meningkat. Sebaliknya, peresapan haba LDH sebagai fungsi terhadap suhu pengkalsinan menghasilkan hubungan linear dan kecerunan yang di perolehi dari data tersebut menunjukan penggantungan antara peresapan haba dan kandungan air dalam LDH di bawah suhu 200 °C. Pada suhu 180 °C ke atas, kelakuan peresapan haba adalah disebabkan oleh fasa ZnO dalam LDH. Peresapan haba LDH sebagai fungsi terhadap nisbah molar menghasilkan hubungan tidak linear. Ia di sebabkan oleh pembentukan fasa-fasa lain (ZnO dan $ZnAl_2O_4$) dalam LDH apabila nisbah molar berkurangan atau nilai pH meningkat.

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I certify that a Thesis Examination Committee has met on 18 September 2012 to conduct the final examination of Abdullah Ahmed Ali Ahmed on his thesis entitled "Synthesis and Characterization of Zinc-Aluminium Layered Double Hydroxide Nanocomposite Prepared Via Coprecipitation Method" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

Members of the Examination Committee are as follows:

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This thesis was submitted to the senate of Universiti Putra Malaysia and has been acceptance fulfillment of the requirement for the degree of Doctor of Philosophy. The members of the supervisory Committee were as follow:

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DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institutions.

ABDULLAH AHMED ALI AHMED
Date: 18 September 2012

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