UNIVERSITI PUTRA MALAYSIA

SYNTHESIS AND CHARACTERIZATION OF ZINC- AND MAGNESIUM-ALUMINIUM LAYERED DOUBLE HYDROXIDE NANOCOMPOSITE INTERCALATED WITH SODIUM DODECYL SULFATE

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By

SAMANEH BABAKHANI

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

June 2014

This thesis is dedicated with gratitude and love to

My lovely mother and father

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

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Chairman: Prof. Zainal Abidin Talib, PhD
Faculty: Science

The co-precipitation method was employed to prepare Zn/Al–NO_3–LDH and Mg/Al–NO_3–LDH at molar ratios of Zn^{2+}/Al^{3+} and Mg^{2+}/Al^{3+} of 2, 3 and 4. The pH was fixed at 7 for Zn/Al-LDH samples and 10 for Mg/Al–LDH samples. Sodium dodecyl sulfate (SDS) was intercalated to Zn/Al–LDH and Mg/Al–LDH to form a new organic–inorganic nanocomposite (LDH–SDS). The concentration of SDS solution used was 0.2 M, 0.4 M and 0.8 M in different molar ratio, Zn^{2+}/Al^{3+} and Mg^{2+}/Al^{3+}= 2, 3 and 4 at pH =10. The structural, textural, optical, thermal and morphological properties of the resultant nanocomposites were investigated. Electron spin resonance (ESR) spectra of samples were also studied.

Analysis of the XRD spectra of LDH and LDH-SDS samples showed that the crystallite size was in the range of 23–51 nm for Zn/Al series and 7-44 nm for Mg/Al series, which confirmed that the pure and intercalated LDH were nanocomposite. This is corroborated by the results of unit cell parameters (*a* and *c*) which showed that the construction of LDH resulted in nanolayers. The shifting in the basal spacing for LDH–SDS samples to around 2.52–2.60 nm comparing with 0.79 nm for Mg/Al–NO_3–LDH and 2.54–2.61 nm comparing with 0.89 nm for Zn/Al–NO_3–LDH indicated the SDS intercalation within the galleries.

Optical band gap of the samples was calculated using Kubelka-Munk model from UV-Vis-NIR Diffuse reflectance spectroscopy. Due to the presence of different phases in LDH, more than one energy gaps were obtained in diffuse reflectance spectroscopy of the samples for LDH and LDH–SDS samples. The values of E_{g1} and E_{g2} were found around 4.8 eV and 3.75 eV for Zn/Al and MgrAl–LDH (r = 2, 3 and 4) which can be attributed to the presence of NO_3^- groups in the LDH interlayer. For MgrAl–LDH–SDS samples with different concentration of SDS and molar ratio (r = 2, 3 and 4), the values of E_{g1} and E_{g2} were observed to increase to around 5.2 eV and 4.1 eV. Consequently, for ZnrAl–LDH–SDS samples in different concentration of SDS, the band gap energy of E_{g1} and E_{g2} were found to increase to 5.2 eV and 4.1 eV for r = 2 and 5.1 eV and 3.9 eV for r = 3. When r = 4, E_{g1} and E_{g2} were decreased to 4.3 eV and 3.2 eV for LDH–SDS with 0.2 M of SDS. For LDH–SDS with 0.4 M and 0.8 M of SDS, only one energy gap at around 3.23 eV was observed. These E_g values can be due to the electronic transition of the oxygen from the DS anion (SO_4^{2-}) from the interlayer and a nearby Al nucleus ($I = 5/2$) from the LDH sheets.

The electron spin resonance (ESR) spectra of LDH were comprised of a broad signal with g-factor between 1.9323 and 2.0187 for MgrAl-LDH and g-factor between 2.06841 to 2.11875 for ZnrAl–LDH which can be caused by the existence of nitrate radicals within LDH interlayer. The ESR spectra of LDH-SDS are observed due to the interaction between a SO_4^{2-} radical from DS anion and a nearby Al nucleus ($I = 5/2$) from the LDH sheets. ESR results for Zn/Al–LDH–SDS samples revealed that the g-factor was decreased comparing with LDH samples. The obtained results for Mg/Al-LDH-SDS samples demonstrated that the g-factor was observed to increase for ratio 2, while it was found to decrease for ratio 3 and 4.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
Sebagai memenuhi keperluan untuk ijazah master sain

SINTESIS DAN PENCIRIAN ZINK/ DAN MAGNESIUM/ALUMINIUM BERLAPIS HIDROKSIDA DUA NANOKOMPOSIT DIINTERKALASI DENGAN NATRIUM SULFAT DODECYL

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Kaedah ko-pemendakan digunakan untuk menghasilkan Zn/Al–NO_3-LDH dan Mg/Al–NO_3-LDH dengan nisbah molar Zn^{2+}/Al^{3+} dan Mg^{2+}/Al^{3+} pada 2, 3 dan 4. pH sampel Zn/Al-LDH dilaraskan pada nilai 7 dan nilai 10 untuk Mg/Al-LD. Sodium dodecyl sulfat (SDS) diinterkalasi dengan Zn/Al-LDH dan Mg/Al-LDH untuk menghasilkan organik-inorganik nanokomposit baharu (LDH-SDS), Kepekatan larutan SDS yand digunakan adalah 0.2 M, 0.4 M dan 0.8 M dengan nisbah nilai molar berbeza Zn^{2+}/Al^{3+} dan Mg^{2+}/Al^{3+} pada 2, 3 dan 4 dengan nilai pH tetap pada 10. Kajian berkenaan struktur, tekstur, sifat morfologi dan terma dilaksanakan keatas sampel nanokomposit paduan menggunakan kaedah pembelauan sinar-X serbuk (PXRD), Inframerah Fourier Transform (FTIR), analisis permeteran graviti haba (TGA-DTG) dan mikroskopi pengimbasan elektron (SEM). UV-Vis-NIR Pantulan resap spektroskopi digunakan untuk menentukan celah jalur tenaga dan mengkaji serapan spekta sampel LDH dan LDH-SDS. Kajian terhadap sampel menggunakan kaedah elektron putaran resonan spektra juga dilaksanakan.

Analisis XRD terhadap sampel LDH dan LDH-SDS yang menunjukkan saiz kristal dalam julat 23-51 nm bagi siri Zn/Al dan 7-44 nm bagi siri Mg/Al mengesahkan bahawa LDH yang di interkalasi dan LDH tulin adalah nanokomposit. Keputusan parameter unit sel (a dan c) yang menunjukkan bahawa LDH yang dihasilkan adalah lapisan nano menyokong keputusan sebelum ini. Peralihan jarak bawah (*basal)* sampel LDH-SDS ke julat 2.52-2.60 nm berbanding dengan 0.79 nm pada Mg/Al–NO_3-LDH dan 0.89 nm pada Zn/Al–NO_3-LDH menunjukkan SDS interkalasi adalah dalam julat sepatutnya.

Celah tenaga optik semua sampel ditentukan menggunakan model *Kubelka-Munk*. Disebabkan kewujudan fasa berbeza dalam LDH, lebih dari satu nilai celah tenaga diperolehi menggunakan kaedah Pantulan resap spektroskopi dari sampel LDH dan LDH-SDS. Nilai Eg1 dan Eg2 Zn/Al dan MgrAl–LDH (r= 2, 3 dan 4) yang diperolehi adalah lebih kurang 4.8 eV dan 3.75 eV dan boleh dikaitkan dengan wujudnya kumpulan NO_3^- dalam lapisan LDH. Sampel MgrAl–LDH–SDS yang berbeza kepekatan SDS dan nisbah molar (r=2, 3 dan 4), didapati Eg1 dan Eg2nya meningkat ke nilai lebih kurang 5.2 eV dan 4.1 eV. Hasilnya, sampel ZnrAl-LDH-SDS yang berbeza kepekatan SDS, jalur celah tenaga Eg1 dan Eg2 didapati meningkat ke 5.2 eV dan 4.1 eV bila r=2 dan 5.1 eV dan 3.9 eV bila r=3. Bila r=4, LDH-SDS yang SDSnya 0.2 M, nilai Eg1 dan Eg2 berkurang ke 4.3 eV dan 3.2 eV. Manakala LDH-SDS yang SDS nya 0.4 M dan 0.9 M hanya satu celah tenaga diperolehi dalam nilai lebih kurang 3.23 eV. Nilai Eg yang diperolehi tersebut adalah disebabkan peralihan elektronik oleh oksigen dari DS anion (SO_4^{2-}) dalam lapisan dan nucleus Al berhampiran (I=5/2) dalam lapisan LDS.

Elektron putaran resonan spectra (ESR) LDH MgrAl-LDH terdiri daripada signal lebar dengan faktor-g antara 1.9323 dan 2.0187 dan ESR spectra ZnrAl-LDH dengan faktor-g antara 2.06841 dan 2.11875 yang disebabkan oleh kewujudan radikal nitrat antara dalam lapisan LDH. ESR spektra LDH-SDS didapati adalah disebabkan interaksi antara radikal SO_4^{2-} dalam anion DS dan nucleus Al berdekatan (I=5/2) dalam lapisan LDH. Keputusan ESR sampel Zn/Al-LDH-SDS menunjukkan bahawa faktor-g berkurang berbanding dengan sampel LDH. Keputusan yang diperolehi dari sampel Mg/Al-LDH-SDS bernisbah 2 menunjukkan faktor-g meningkat sementara bila bernisbah 3 dan 4 faktor-g didapati menurun.

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I certify that a Thesis Examination Committee has met on 9 June to conduct the final examination of Samaneh Babakhani on her thesis entitled " SYNTHESIS AND CHARACTERIZATION OF ZINC- AND MAGNESIUM-ALUMINIUM LAYERED DOUBLE HYDROXIDE NANOCOMPOSITE INTERCALATED WITH SODIUM DODECYL SULFATE" 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 Master of Science.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

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LIST OF ABBREVIATIONS

LDH	Layered Double Hydroxide
HTs	Hydrotalcites
SDS	Sodium dodecyl Sulfate
FE-SEM	Field emission scanning electron microscopy
PXRD	Powder X-ray diffraction
FTIR	Fourier Transform Infrared
T	Temperature
cm	Centimeter
nm	Nanometer
eV	Electron-Volt unit of energy
Eg	Optical band gap energy
Ea	Activation energy
λ	Wavelength
a, c	Lattice parameters of crystal
ω	Angular frequency
h	Hour
min	Minute
θ	Bragg angle
ESR	Electron spin resonance
d_{hkl}	d-spacing in hkl plane
hkl	Miller indices
D	Crystalline size

CHAPTER 1

INTRODUCTION

1.1 Research background

"Nanocomposites are composite materials in which nanoparticles are embedded in a host phase. This is part of the growing field of nanotechnology." (Ghotbi, 2009). The interesting fact is that not only are nanocomposites environmental-friendly, but also, they provide numerous new opportunities in various industrial areas. Different fields of science, study and technology such as physics, chemistry and natural sciences are largely influenced by the application of nanocomposites and their developing technology.

Currently the syntheses of hybrid materials of organic/ inorganic specifically in the field of composite in a nanoscale system (nanocamposite materials) has been given a lot of attention. This is due to the fact that these kinds of materials have exhibited electronic, optical, physical or catalytic properties that are different from their counterparts. Additionally, selecting the proper combination for the guest-host species, the resulting properties could be tailor-made. Layered structure nanocamposite materials may be built by taking apart the layered host and intercalating guest molecules inside.

The material which is made here is named pillared layered structure, inside which the host maybe used as layers to support layers of various entity (Hussein *et al.*, 2002). One ideal host for the organic-inorganic nanohybrid materials or nanocomposites can be a two dimensional layered structure that includes thin crystalline inorganic layers that have a molecular scale thickness of a nanometer range. Layered double hydroxide (LDH) can be named as an example for this structure. Planting various anionic species as guests inside interlayer spaces of the LDH lead to having a growth in the interlayer distance toward a nanometer size dimension that shapes a new nano hybrid material (Ghotbi, 2009). LDHs are currently under spotlight because of their capabilities in industrial and medical applications. They have a key role in the fields of separation process, catalysis, DNA or biomolecule carriers, and drug delivery (controlled drug release). In addition to their role as working nanostructures, they also put on show a large number of electronic and magnetic properties.

LDHs include layers that held hydroxides from different types of metal cations, including a positive total charge that is balanced by intercalation of exchangeable anions inside the hydrated interlayer space. The octahedral units of M^{II} or M^{III} share edges to form infinite sheets. These sheets are stacked on top of each other and are held together by hydrogen bonding. Inorganic/organic anions are inserted among layers with the goal of keeping the charge balance contained; the crystallization water is also widely available inside the interlayer galleries. The ability of anionic exchange of LDHs may be incorporated to bring together the surfactant organic anions inside the interlayer region in an attempt to make organo-LDHs (Zhao *et al.*, 2011).

Intercalation inside a LDH is an activity which breaks down the interactions among the positive charged layers and the primitive interlayer anion, in such a manner that new bonding communication can be formed between the new guest anions and the host. Over the past decade a huge number of LDHs has been investigated both experimentally and theoretically. Various organic anionic have been intercalated inside the interlayer space of the LDHs. Among them are; amino acids, drugs, antibiotics, DNA, heparine (anti-coagulants) which has a short life cycle, etc. LDHs are believed to be a class of materials which are not difficult to synthesize inside the lab, though they are not always found in pure phases. Generally there are various techniques to make LDHs, like ion exchange, co-precipitation, hydrothermal, sol-gel, laser ablation etc. Among these techniques, co-precipitation is most frequently used as it is also the simplest.

For Zn/Al and Mg/Al-layered double hydroxide-sodium dodecyl sulphate (SDS) nanocamposite case, the organic molecular layer of SDS can be taken into account as the guest`s positively charged layer that will be sandwiched between the inorganic layer of Zn/Al-Layered double hydroxide in an attempt to balance the inorganic negatively charged layer of the LDH. This conveys the meaning that we will have a hybrid layer which includes one organic layer sandwiched between two inorganic ones (Costa *et al.*, 2008). This sort of layered materials has the ability to be synthesized indirectly or directly. Over the direct approach, which is also called the spontaneous self-assembly method, the host and the guest forming species are inside the mother liquor, the activity which will be proceeded by aging process in an attempt to form a well-crystalized nanocamposite. In the indirect approach, the host should be first prepared, and afterwards the further treatment or modification of the host takes place and in the end intercalation of the guest molecule into the host layers finishes the process (Hussein *et al.*, 2002).

1.2 Problem statement

LDH compounds are technologically considered as one of the most promising materials due to their large number of preparation/composition variables, low cost, and relatively easy preparation. Recently, a large amount of commercial and academic work on LDH materials field has been done and it is remarkable that still more remain to be done in order to apply completely their potential applications.

Since organic–inorganic hybrid materials have improved and better properties rather than their counterparts, development of these types of materials provides excellence aspects of applications in different areas of technology and science. This also is because their property can be tailor-made to special application such as in photochromic coating, photochemical reaction and selective optical transmission, to name a few. For the formation of a nanolayered composite of organic-inorganic hybrid type, or the so-called nanocomposite materials, LDHs or Hydrotalcite-like material can be one of the popular inorganic hosts for the formation of an organic–inorganic hybrid type. Several studies have focused on intercalation of various dye molecules, especially organic dyes into the layered inorganic lamella, in particular anionic clays for different applications and purposes (Hussein *et al.*, 2004).

Considering the above findings, an idea to study the properties of novel nanocomposites with intercalated anion has been generated. Sodium dodecyl sulfate has been specially chosen to study the physico-chemical properties of the obtained nanocomposite. We report here the synthesis of Zn/Al and Mg/Al-LDHs by coprecipitation method, intercalation of sodium dodecyl sulfate into the interlayer of the LDHs, a comparative study of the UV absorption ability of the LDH-SDS nanocomposites, ESR spectrum of the resulted nanocomposites and the effect of intercalation on the thermal stability of the SDS.

1.3 Hypothesis of study

In the current work, Zn/Al-LDH and Mg/Al-LDH will be synthesized via coprecipitation method. Sodium dodecyl sulphate (SDS) has been chosen to be intercalated into the interlayer of the Zn/Al-LDH and Mg/Al-LDH using coprecipitation method to form a new organic–inorganic nanocomposite. The anion will intercalate in the interlayer region, replacing nitrate ion thus expanding the basal spacing. The structural and morphological properties of the resultant nanocomposites were investigated. The optical band gap and absorption spectra of samples were studied. Thermal properties and ESR spectra were also obtained for the SDS-LDH nanocomposites. Results from the powder X-ray diffraction (PXRD), Optical absorption and band gap (UV–VIS–NIR diffuse reflectance), field emission scanning electron microscopy (FESEM), Fourier Transform Inferared (FTIR), and also Electron Spin Resonance (ESR) are discussed. It is assumed that the intercalated SDS will affect the properties of the produced nanocomposites. The effect of Zn/Al and Mg/Al molar ratio and SDS concentration on the resulted nanocomposites are investigated.

1.4 Objectives of the study

The objectives of this study are:

1) To intercalate the sodium dodecyl sulfate into the Zn/Al-NO_3-LDH and Mg/Al-NO_3-LDH using chemical precipitation method in different molar ratio (Zn/Al and Mg/Al of 2, 3 and 4) and SDS concentration (0.2M, 0.4M and 0.8M) and to investigate the structural, textural and morphological properties of the resulted nanocomposite (using XRD, FTIR and SEM).

2) To measure the optical band gap energy of LDH and LDH-SDS nanocomposites which relates to the evaluation of optical properties and photocatalytic activity.

3) To study the electron spin resonance (ESR) of samples in order to evaluate the magnetic activity of LDH phase.

4) To investigate the thermal properties of material which play an important factor in some application of LDH.

1.5 Outline of the study

A brief introduction on nanocomposites especially intercalated-type nanocomposites and important methods which are used to prepare LDHs were explained in Chapter 2. Because the coprecipitation method has been used in this work, it was reported in more details. Previous studies which are related to the structural, textural, morphological, optical and thermal properties and the electron spin resonance (ESR) studies of Zn/Al and Mg/Al-LDH and different intercalated LDHs have also been presented.

To understand the behaviour of layered double hydroxides (LDHs), it is important to study the relationship between the observed material properties and the underlying physical phenomena behind those properties. Due to the ability of LDHs to intercalate anionic compounds, these compounds can be used for many applications such as: catalysts, tailor making adsorbents, sensors, precursor materials for oxides, for removing SOx and NOx from combustion flue gas and microorganisms (bacteria and viruses) from water, and for drug delivery. These applications depend on structural, photocatalysis, magnetic and thermal properties of the material. Theoretical background about these properties of LDHs and the related characterization techniques is presented in Chapter 3.

The results and discussion of this work are presented in two separated categories of data in Chapter 5. The first one was represented by the synthesized samples of Zn/Al-LDH and LDH-SDS at different Zn^{2+}/Al^{3+} molar ratios (2, 3 and 4) and different SDS concentration (0.2, 0.4 and 0.8 M), while the second category is for Mg/Al-LDH and its LDH-SDS at different Mg^{2+}/Al^{3+} molar ratios (2, 3 and 4) and different SDS concentration (0.2, 0.4 and 0.8 M). For each category, the available characterizations have been studied and discussed.

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