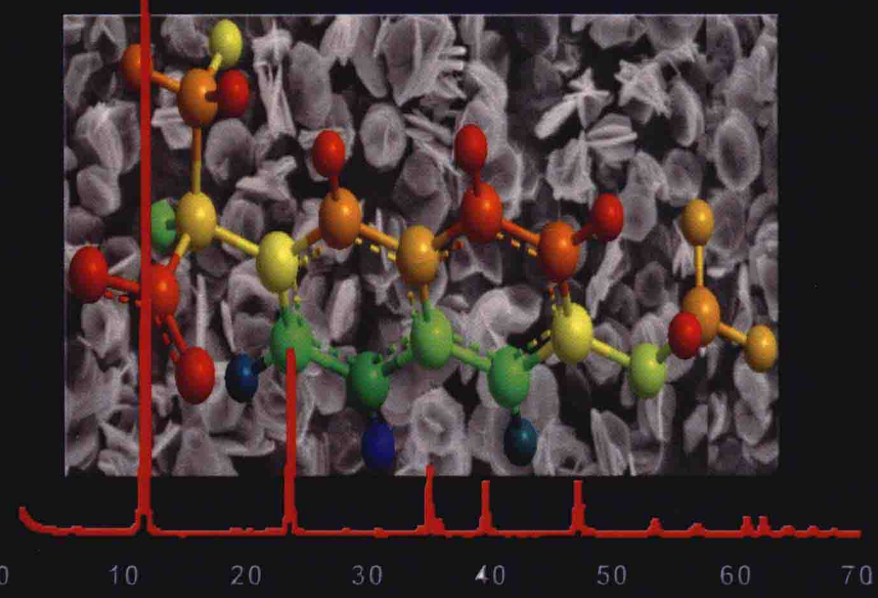
Recent Advances in Layered Double Hydroxide-Based Composites

Synthesis, Properties and Potential Applications



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Chemistry Research and Applications

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CHEMISTRY RESEARCH AND APPLICATIONS

RECENT ADVANCES IN LAYERED DOUBLE HYDROXIDE-BASED COMPOSITES

SYNTHESIS, PROPERTIES AND POTENTIAL APPLICATIONS

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AND

INAS HAZZAA HAFEZ

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PREFACE

Naturally occurring materials such as layered materials along with artificial layered materials produced industrially, are receiving a great deal of attention in the field of nanotechnology, in particular hybrid and composite research fields. They have a chemical composition and particular structure that give them specific properties or functions in relation to their surroundings or their formation conditions. Layered double hydroxide (LDH) is an important kind of the layered materials. They are formed in nature under certain conditions, and can be studied either in their original state or after being modified. LDH is considered to be one of the most important materials in the field of organic-inorganic composite research.

The fact that this book issued is due the fast progress in the field of LDH and its composites, and also how important the LDH research is in the entire world. Therefore, it is an appropriate time to compile a book presenting a comprehensive review of the current status of LDH, especially focused on its recent advances. In this book, we aim to present an overview of the recent advancements of research in LDH in the areas of synthesis, properties and potential applications in fields such as, additives of polymers, catalysis, adsorption, water purification, medicine, pharmaceutics, photochemistry, biochemistry, and electrochemistry.

This book consists of a number of chapters. In the second chapter, we surveyed the different synthetic techniques of LDH and its composites. The third chapter summarized the LDH properties including solubility and swelling properties, acid-base properties, specific surface area and factors affecting it, pillaring character, crystallite structure factors affecting it, particle size properties, thermal properties, memory effect property and factors affecting it, anion exchange capacity, biomedical properties, photocatalytic properties, photoluminescence properties, magneto-optical properties, and the photochromism phenomena. The fourth, fifth and sixth chapters focused on the different applications of LDH mentioned above.

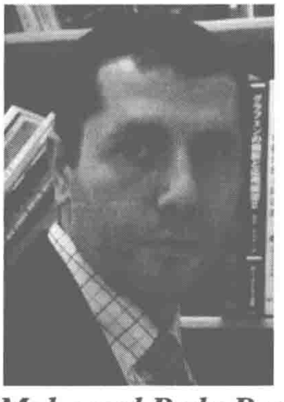
We hope this book will be beneficial for the scientific community including students, teachers and researchers. On the other side of this book, I would like to thank my dear wife and my children Ayten, Lama, Perla, and Yuki for their unfailing and understanding during the preparation of this book.

At the same time, I would like to thank my parents who are looking forward to seeing me.

Also, sincere thanks to all the members of Tanta University, Damanhour University, and Kyushu University for their support during the preparation of this book.

Mohamed Reda Berber
Inas Hazza Hafez

AUTHORS' BIOGRAPHIES



Dr. Mohamed Reda Berber

After graduating from the Chemistry Department, Faculty of Science, Tanta University, Egypt in 1997, *Dr. Mohamed Reda Berber* obtained his PhD from Tokushima University, Japan, followed by a post-doctoral fellowship at Kyushu University, Japan. Now, he is an assistant professor at the same University.

Dr. Berber carried out a scientific research for more than 19 years including the research of natural polymers, synthetic polymers, organic-inorganic composites, polymer composites and polymer electrolyte membrane fuel cells (PEMFCs). During that period, he co-authored two academic books, and published 30 papers in refereed international journals and more than 71 conference papers.

Dr. Berber is internationally recognized for his work in chemistry. His smart sensitive polymeric material work was selected as one of the *Hot Topics in Polymer Science Japan* in 2010. Also, very recently his work in PEMFC was highlighted in *NATURE.*

Dr. Berber is an active member of the American Chemical Society (ACS) and the Society of Polymer Science, Japan (SPSJ). He is a potential reviewer in many international journals including International Journal of Nanomedicine, Journal of Nanobiotechnology, Current Nanoscience, Journal of solid state Chemistry, Journal of Applied Mechanical Engineering, International Journal of pharmaceutics, Toxicological and Environmental chemistry, International Journal of Molecular Sciences, Chemistry Central Journal, and Applied Clay Science.

In recognition of his achievements in science, his bio-data is published in Marquis *Who's Who* in 2011 and 2014. Also, he dedicated in the year 2012 to the world forum sixth edition, OXFORD, as one of the great minds of the 21st century. In addition, he represented Egypt in the advisory board of the International Association of Hydrogen Energy (IAHE) during the 20th World Hydrogen Energy Conference held in South Korea.

Dr. Inas Hazza Hafez

Dr. Inas Hazza Hafez graduated from Alexandria University, Egypt, and obtained her master degree in Agriculture Engineering from the department of Water Resources and Agriculture Engineering of the same university. *Dr. Inas* received her PhD in Polymer Science and Nanotechnology from The University of Tokushima, Japan, followed by a post-doctoral fellowship at Kyushu University, Japan.

Dr. Inas is an expert on agriculture engineering, in particular irrigation systems, polymer-soil applications, polymer nanocomposite applications, catalysis and polymer electrolyte membrane fuel cells. She co-authored two academic books, and published more than 20 papers in refereed international journals and more than 50 conference papers. Currently she is working at International Institute for Carbon-Neutral Energy Research (I^2CNER), Kyushu University in the field of fuel cells and their environmental applications.

Dr. Inas is a member of the Society of Polymer Science, Japan (SPSJ). In recognition of her scientific achievements, her bio-data is published in Marquis *Who's Who* in 2015.

ABBREVIATIONS AND SYMBOLS

AA	Acrylic acid
AEMFCs	Anion-exchange membrane fuel cells
AFM	Atomic force microscopy
Al	Aluminium
As	Arsenic
ATP	Adenosine triphosphate
AQS	Anthraquinone sulfonate anion
BEHP	Bis(2-ethylhexyl)hydrogen phosphate
BET	Brunauer–Emmett–Teller
Ca	Calcium
Ce	Cerium
CFs	Carbon fibers
CHN	Carbon, hydrogen and nitrogen content
Cl	Cloride
CO_3	Carbonate
Co	Cobalt
β-CMCD	Carboxy-methyl beta-cyclodextrin
CNT	Carbon nanotubes
Cr	Chromium
Cu	Copper
CV	Conventional coprecipitation technique of LDH
CV	Cyclic voltammetry
d	The spacing between each lattice
D_{003}	Crystallite size of LDH
D	Dielectric constants
DDBS	Dodecylbenzenesulfonate
DEFCs	Direct ethanol fuel cells
DHBC	Double hydrophilic block copolymers
DIP	Digital image processing
DMF	Dimethyl formamide
DMT	Dimethyl terephthalate
DODMA	Dioctadecyldimethylammonium
DSCs	Dye-sensitized solar cells

EDTA	Ethylene diamine tetra acetic acid
EG	Ethyleneglycol
EXAFS	Extended X-ray absorption fine structure spectroscopy
Fe	Iron
FESEM	Field emission scanning electron microscopy
FTIR	Fourier transform infrared spectroscopy
FFT	Fast Fourier transform analysis
FWHM	Full width at half-maxima
GA	Gibberellic acid
HAAs	Haloacetic acids
HPIC	Hybrid polyion complex
HRTEM	High resolution transmittance electron microscopy
IBU	Ibuprofen
ICP-AES	Inductively coupled plasma atomic emission spectroscopy
ICP-OES	Inductively coupled plasma optical emission spectroscopy
IPDI	Isophorone diisocyanate
IPCE	Incident-photon-to-current-conversion efficiency
LDH(s)	Layered double hydroxide(s)
Li	Lithium
$M^{(II)}$	Divalent metal
$M^{(III)}$	Trivalent metal
MCD	Magnetic circular dichroism
MEAs	Membrane assemblies
Mg	Magnesium
MMO	Mixed metal oxides
MMT	Montmorillonite
Mn	Manganese
MW	Microwave radiation
NaDDS	Sodium dodecyl sulfate
NMR	Nuclear magnetic resonance
NO_3	Nitrate
Ni	Nickel
TEM	Transmittance electron microscopy
THMs	Bromochloro-trihalomethanes
OER	Oxygen evolution reaction
ORR	Oxygen reduction reaction
PAA	Polyacrylic acid
PAM	Polyacrylamide
PEGS	Polyoxyethylene sulfate
PEC	Photoelectrochemical
PL	Photoluminescence
PMP	Phenoxymethylpenicillin
PS	Polystyrene beads
PSS	Poly(sodium styrene 4-sulfonate)
PVA	Polyvinylalcohol
PXRD	Powder X-ray diffraction

RB19	Remazol Blue 19
SDS	Sodium dodecyl sulfate
SEM	Scanning electron microscopy
Sn	Tin
SSA	Specific surface area
Ti	Titanium
TPB	Triple phase boundary
U	Urea hydrothermal treatment of LDH
V_{OC}	Open-circuit voltage
WHO	World Health Organization
XPS	X-ray photoelectron spectroscopy
Y	Interlayer anion
Zn	Zinc
ZnAc	Zinc acetate

CONTENTS

Chapter 1

GENERAL INTRODUCTION OF CLAY MATERIALS

1. HISTORICAL BACKGROUND OF CLAYS

Clays are fine-grained soil distinguished by its size and mineralogy. It combines one or more clay minerals, i.e., alkali metals, alkaline earths, and other cations with traces of metal oxides and organic matter. With regard to the origin and formation of clays as assessed principally by X-ray diffraction and microscopic techniques, there are three principal processes to account for the genesis of clay minerals, which may occur at different points in the geochemical cycle including weathering or soil formation at the earth's surface. These processes are: a- detrital inheritance whereby, for soils, clay minerals are inherited from pre-existing parent rock or weathered materials; b- transformation where the essential silicate structure of the clay mineral is maintained to a large extent, but with major change in the interlayer region of the structure; and c- neoformation, where the clay mineral forms through crystallization of gels or solutions. [1]

2. TYPES OF CLAYS

Clays are divided into two main groups depending on their ionic character; cationic clays and anionic clays. [2]

2.1. Cationic Clays

Cationic clays are widely occurring in nature, having negatively charged layers with cations in the interlayer space to balance the net negative charge. They are generally prepared starting from the clay minerals. [3] The most common cationic clay is smectite, in particular, montmorillonite which is a hydrated magnesium and aluminum silicate with sodium ion or calcium ion as interlayer cations. The interlayer cation can be easily replaced by a foreign cation, thus, montmorillonite have received a great deal of attention. Montmorillonite has different applications in the different fields, including medicine, pharmacy, food production, catalysis, surfactants, and agriculture. It is also common as nanofiller to improve the mechanical and the thermal properties of the polymers. [2]

2.2. Anionic Clays

Anionic clays are natural or synthetic materials based on metal hydroxide layers with a net positive charge balanced by water and exchangeable anions. They also identified as intermediates in weathering of serpentines and basalts. [4] Anionic clays can be defined by their chemical composition, basal spacing and stacking sequence. They exhibit quite large variation in the chemical composition of the metal hydroxide layers and are capable of incorporating a wide range of cations in these layers. Basically there is no restriction on the anion type used in the exchange process, which makes anionic clays an attractive material for the different applications. [4] There are different kinds of anionic clays depending on the composition and the polytype form of the minerals used during the formation of the clay. Figure 1, summarizes most of the naturally occurring anionic clays. [5, 6]

2.2.1. Hydrotalcite

Hydrotalcite is the most common type of the anionic clays. It is a natural mineral with a white color and pearl like luster. Hydrotalcite named in 1842 by Carl Christian Hochstetter due to its high water content (Hydro-) and to its resemblance to talc. It is a compound of magnesium and aluminum with a layer structure, having the following composition $Mg_6Al_2(OH)_{16}CO_3.4H_2O$. Kyowa Chemical Industry of Japan has noted this unique structure of hydrotalcite and has become the first in the world to succeed in the industrial synthesis of hydrotalcite in 1966. [3] Kyowa's synthetic hydrotalcite was developed first as a medical antacid agent. It has been sold by globally known pharmaceutical firms and continues to be widely supplied to various nations all over the world. [3] on the basis of X-ray analysis, hydrotalcites are stacked in various ways, which gives rise to a variety of possible polytypes structures. If the opposing OH groups lie vertically above one another, an interlayer with a trigonal prismatic arrangement results, whilst if they are offset, an octahedral arrangement is formed. There are three possible two-layer polytypes with hexagonal stacking of the layers, donated $2H_1$, $2H_2$, and $2H_3$, where the $2H_1$ polytype has all prismatic interlayers and the $2H_2$ polytype has all octahedral interlayers, whilst both types of interlayers are present in the $2H_3$ polytype. There are nine possible three-layer polytypes, of which two have rhombohedral symmetry-$3R_1$ and $3R_2$, whilst the remaining seven ($3H_1$-$3H_7$) have hexagonal symmetry. [7, 8]

Mineral	Chemical composition	Unit cell parameters		Symmetry
		a (nm)	c (nm)	
Hydrotalcite	$Mg_6Al_2(OH)_{16}CO_3.4H_2O$	0.3054	2.281	3R
Manasseite	$Mg_6Al_2(OH)_{16}CO_3.4H_2O$	0.31	1.56	2H
Pyroaurite	$Mg_6Fe_2(OH)_{16}CO_3.4H_2O$	0.3109	2.341	3R
Sjogrenite	$Mg_6Fe_2(OH)_{16}CO_3.4H_2O$	0.3113	1.561	2H
Stichtite	$Mg_6Cr_2(OH)_{16}CO_3.4H_2O$	0.31	2.34	3R
Barbertonite	$Mg_6Cr_2(OH)_{16}CO_3.4H_2O$	0.31	1.56	2H
Takovite	$Ni_6Al_2(OH)_{16}CO_3.4H_2O$	0.3025	2.259	3R
Reevesite	$Ni_6Al_2(OH)_{16}CO_3.4H_2O$	0.3081	2.305	3R
Meixnerite	$Mg_6Al_2(OH)_{18}.4H_2O$	0.3046	2.292	3R
Coalingite	$Mg_{10}Fe_2(OH)_{24}CO_3.2H_2O$	0.312	3.75	3R

Figure 1. Composition, crystallographic parameters and symmetry for anionic clays.