LAYERED METAL HYDROXIDES: EXFOLIATION ASSISTED BY SUGAR MOLECULES AND PHYSICOCHEMICAL CHARACTERISATION OF THE NANOSHEETS

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by

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LIST OF SYMBOLS

gram g 0 degree °C degree Celsius h hour percentage % micrometre μm m metre grams per litre g/L g/cm³ grams per cubic metre g/m^2 grams per square metre g/mol grams per mol g/h grams per hour Kelvin per second K/s kHz kilohertz milliequivalents per gram meq/g m^2/g square metre per gram milligrams per gram mg/g milligrams per millilitre mg/mL mA/cm² milliampere per square centimetre cm²/mg square centimetre per milligram mL millilitre

min	minute
mV	millivolt
Mpa	MegaPascal
Nm	nanometre
Rpm	revolutions per minute
V	volt
wt%	weight percentage
W	watts

LIST OF ABBREVIATIONS

AEC	Anion exchange capacity	
AFM	Atomic force microscopy	
Al(NO3)2.9H2O	Aluminium nitrate nanohydrate	
AgS2	Silver sulfide	
Bi2Te3	Bismuth telluride	
BMIMSCN	1-butyl-3-methylimidazolium thiocyanate	
BET	Brunauer-Emmett-Teller	
BM	Ball-milling	
CF	Centrifugation	
СВ	Carbon black	
CVD	Chemical vapor deposition	
Cu9S5	Digenite	
CHP	Cyclohexylpyrrolidone	
CCI4	Carbon tetrachloride	
СМС	Carboxymethyl cellulose	
DMF	Dimethylformamide	
DMSO	Dimethyl sulfoxide	
DSC	Differential scanning calorimetry	
EAN	Ethylammonium nitrate	
FTIR	Fourier-transform infrared spectroscopy	
GaS	Gallium(II) sulfide	
GCE	Glassy carbon electrode	

GO	Graphene oxide	
GBL	γ-butyrolactone	
h-Bn	hexagonal boron nitride	
H2SO4	Sulfuric acid	
H3PO4	Phosphoric acid	
HCIO4	Perchloric acid	
H2C2O4	Oxalic acid	
H2O2	Hydrogen peroxide	
HO-	Hydroxyl ions	
HER	Hydrogen evolution reaction	
ILs	Ionic liquids	
IPA	Isopropyl alcohol	
InSe	Indium(II) selenide	
INH	Isoniazid	
LDHs	Layered double hydroxides	
LZHs	Layered zinc hydroxides	
LPE	Liquid phase exfoliation	
LSHs	Layered single metal hydroxides	
LBMS	Layered basic metal salt	
MoS2	Molybdenum sulfide	
MgBr2	Magnesium Bromide	
MnO2	Manganese oxide	
MoO3	Molybdenum trioxide	
Mg(OH)2	Brucite	

MD	Molecular dynamics	
Mg(NO ₃) ₂ .6H ₂ O	Magnesium nitrate hexahydrate	
NMP	N-methylpyrrolidone	
NaOH	Sodium hydroxide	
O2 ²⁻	Peroxide ions	
PbI ₂	Lead(II) oxide	
3R	Rhombohedral	
rGO	Reduced graphene oxide	
REACH	Registration, Evaluation, Authorisation and Restriction of	
	Chemicals regulation	
Sb ₂ Se ₃	Antimony triselenide	
SOBS	4-octyl benzenesulfonate	
SOS	Sodium octyl sulfate	
SDS	Sodium dodecyl sulfate	
SEM	Scanning electron microscopy	
2D	Two-dimensional	
3D	Three-dimensional	
TGA	Thermogravimetric analysis	
TEM	Transmission electron microscopy	
TMDs	Transition metal dichalcogenides	
TEMPO	2,2,6,6-tetramethyl-1-piperidinyloxy	
Et ₃ NH+	Triethylammonium ions	
VOT	Volatile organic compound	
WSe ₂	Tungsten diselenide	
XRD	X-ray diffraction	

Zn(NO₃)₂.6H₂O

LOGAM HIDROKSIDA BERLAPIS: PENGELUPASAN DIBANTU OLEH MOLEKUL GULA DAN CIRI-CIRI FIZIKOKIMIA LEMBARAN NANO

ABSTRAK

Pengelupasan bahan logam hidroksida berlapis adalah sangat baik untuk pembentukan lapisan tunggal hidroksida berganda (LDH) dan kepingan nano zink hidroksida (LZH) berlapis kerana sifat kimia, haba, optik dan biologinya yang unik. Dalam kajian ini, pengelupasan lapisan berganda hidroksida (LDH) dan zink hidroksida berlapis (LZH) dilakukan menggunakan molekul gula sebagai agen pengelupasan dalam DMSO dan air ultratulen. Serakan sinar X-ray (XRD) mencadangkan bahawa LDH Berjaya dieksfoliasi dan membentuk nanosheet lapisan tunggal, ditunjukkan oleh pembentukan puncak tunggal. Ia ditunjukkan bahawa corak XRD LDH menggunakan sukrosa 1g dalam DMSO melalui pemandakan serentak, rekonstruksi, dan hidroterma menunjukkan corak pembelauan terbaik dengan hanya satu punca yang terbentuk dalam semua sampel terkelupas. Maklumat struktur LDH terkelupas dalam tiga fasa berebeza dikaji lebih lanjut menggunakan XRD untuk mendedahkan tahap proses pengelupasan. Kami memeriksa fasa kristal LDH dalam pelbagai pengelupasan cecair; ampaian, ampaian separuh kering dan sampel pepejal kering. Data XRD menunjukkan satu puncak yang luas untuk semua sampel terkelupas LDH pada $2\theta = 23.9$, 22.4, dan 22.3° masing-masing, yang sepadan dengan ciri (006) pantulan basal bagi lapisan tunggal LDH. Sebaliknya, hanya corak XRD LZH yang dikelupas dengan 1g sukrosa dalam air ultratulen melalui hidroterma mempamerkan puncak tunggal manakala pemendakan serentak dan rekonstruksi tidak. Oleh itu,

hanya kaedah hidroterma dalam LZH menunjukkan pembentukan helaian nano.

Spektroskopi Fourier terubah inframerah (FTIR) mengesahkan lagi pengelupasan LDH dan LZH. Puncak keamatan yang lebih tinggi di rantau 1000-1020 cm⁻¹ untuk sampel terkelupas LDH menunjukkan kejayaan pengelupasan molekul gula dalam interlayer LDH. Jalur baru yang terbentuk dalam LZH terkelupas menunjukkan pengelupasan molekul gula ke dalam lapisan antara LZH. Selain itu, analisis termal mempamerkan bahawa sifat termal semua sampel terkelupas dipertingkatkan berbanding dengan LZH tulen dan tulen LDH, mungkin disebabkan oleh lebih banyak peratusan kehilangan jisim dan peningkatan suhu semasa proses pengelupasan. Perlu diingat bahawa analisis BET mungkin menunjukkan pengelupasan LDH and LZH yang berjaya. Berbanding dengan LDH tulen, LDH yang dieksfoliasi dengan sukrosa menunjukkan cawangan penjerapan yang luas disebabkan oleh peningkatan jarak basal semasa pertukaran ion nitrat dengan molekul gula ke dalam lapisan antara LDH. Pengurangan dalam isipadu liang diperhatikan untuk LZH apabila sucrose dieksfoliasi di antara lapisan LZH. Analisis TEM membuktikan pembentukan nanosheet dan zarah seperti sfera untuk LDH and LZH. Kerja ini menunjukkan bahawa lembaran nano LDH dan LZH boleh diperoleh dengan menggunakan biomolekul hijau melalui kaedah sinetik mudah.

LAYERED METAL HYDROXIDES: EXFOLIATION ASSISTED BY SUGAR MOLECULES AND PHYSICOCHEMICAL CHARACTERISATION OF THE NANOSHEETS

ABSTRACT

The exfoliation of layered metal hydroxides is highly favourable for the formation of single layer layered double hydroxide (LDH) and layered zinc hydroxide (LZH) nanosheets due to their unique chemical, thermal, optics, and biological properties. In this study, the exfoliation of layered double hydroxide (LDH) and layered zinc hydroxide (LZH) were performed using sugar molecules as an exfoliating agent in DMSO and water. The X-ray diffraction (XRD) suggest that LDH were successfully exfoliated and formed single layer nanosheet, indicated by the formation of single peaks. It is demonstrated that XRD patterns of LDH using 1g sucrose in DMSO via co-precipitation, reconstruction, and hydrothermal show the best diffraction pattern with only a single peak formed in all the exfoliated samples. The structural information of the exfoliated LDH in three different phases is further studied using XRD to reveal the extent of the exfoliation process. We examined the crystalline phase of LDH in different stages of liquid exfoliation; suspension, semi-dry suspension and dried solid samples. XRD data shows one broad peak for all the LDH exfoliated samples at $2\theta = 23.9,22.4$, and 22.3° respectively, which correspond to the characteristic (003) basal reflection of LDH single layers. These single peaks indicate the formation of LDH nanosheets. On the other hand, only XRD pattern of LZH exfoliated with 1g sucrose in water via hydrothermal exhibit the single peak while coprecipitation and reconstruction are not. Thus, only hydrothermal method in LZH indicates formation of nanosheets. Fourier transform infrared (FTIR) spectroscopy

further confirms the exfoliation of LDH and LZH. The higher intensity peak at the region 1000-1020 cm⁻¹ for LDH exfoliated samples indicates the successful exfoliation of sugar molecules in the interlayer of LDH. The new bands formed in exfoliated LZH indicates the exfoliation of sugar molecules into interlayer of LZH. Besides, thermal analysis exhibits that the thermal properties of all the exfoliated samples are enhanced compared to the LDH pristine and pure LZH, possibly due to a higher percentage of mass loss and increased temperature during exfoliation process. It is worth noting that Brunauer-Emmett-Teller (BET) analysis might indicate successful exfoliation of LDH and LZH. Compared to LDH pristine, LDH exfoliated with sucrose shows a broad adsorption branch due to the increase in basal spacing during the exchange of nitrate ions with sugar molecules into the interlayer LDH. A decrease in pore volume was observed for LZH when sucrose was exfoliated between the layers of LZH. Transmission electron microscopy (TEM) analysis proved the formation of nanosheets and spherical-like particles for LDH and LZH. This work demonstrates that LDH and LZH nanosheets can be obtained by using green biomolecules through simple synthetic methods.

CHAPTER 1

INTRODUCTION

General background

Nanotechnology has been one of the emerging technologies for the past 20 years. Richard Feynman, an American Physics is known to be the father of nanotechnology. In 1959, he discussed the principles and concepts of nanotechnology in a talk titled "There is Plenty of Space at the Bottom" (Buzea et al., 2007). In 1974, Tokyo Science University Professor Norio Taniguchi, in his paper, defined "nanotechnology" as primarily consisting of the processing, separation, consolidation, and deformation of materials by one atom or one molecule (Bayda et al., 2020). This forthcoming nanotechnology leads to the development of nanomaterials especially two-dimensional (2D) materials. A class of 2D materials called layered material hydroxides nanosheets has drawn much interest in nanotechnology because of its unique characteristics and potential applications.

Layered double hydroxide (LDH) are also known as hydrotalcite (Figure 1.1), are a class of ionic lamellar compounds made up of layers of positively charged hydroxide with charge-balancing anions and water molecules in between the layers (Wu et al., 2022). LDH are cationic layers with 'brucite-like' structures that belong to the anionic clay family. Trivalent cations added to the layers give the nanosheets an overall positive charge (Hobbs et al., 2018). LDH nanosheets have a large surface area, which makes them perfect for application in catalysis, drug delivery, photonics, magnetics, and electronics (Arrabito et al., 2020). Additionally, they are effective carriers for delivering macromolecules into intact plant cells (Bao et al., 2016). LDHs can be easily modified to suit particular purposes and can be synthesised in huge quantities (Arrabito et al., 2020). Recent studies have been focused on improving the synthesis of LDH nanosheets and recognizing their properties. For example, Wang and O'Hare produced a large-scale synthesis of widely distributed LDH powders containing delaminated single-layer nanosheets (Arrabito et al., 2020). Scarpellini et al. examined the morphology of Zn/Al LDH nanosheets produced on aluminium thin films (Arrabito et al., 2020). Li et al. established a controlled synthesis process to scale up the manufacturing of monolayer LDH nanosheets, while Hobbs et al. examined how LDHs changed structurally using in situ TEM analysis (Wu et al., 2022; Hobbs et al., 2018). LDH nanosheets offer great potential for sustainable agriculture and the environment due to their ability to remove heavy metals and other contaminants from the soil and water (Cavani et al., 1991). They are also being researched for their potential function in energy conversion and storage ("Themed issue: layered materials: structure and properties," 2009). Overall, LDH nanosheets are promising materials with numerous potential uses in nanotechnology.



Figure 1.1. Crystal structure of hydrotalcite (Gutowski et al., 2008)

On the other hand, layered zinc hydroxide (LZH) are also a type of layered material nanosheet with unique characteristics and potential applications. LZH are made up of neutral zinc hydroxide layers. These layers contain octahedrally and tetrahedrally coordinated Zn ions and water in the interlayer space (Mishra et al., 2018). Several studies on LZH include: i) A sequence of uniformly distinctive three-dimensional (3D) structures made up of layered zinc hydroxide (LZH) were created using a hydrothermal process (Song et al., 2016). ii) The removal of chromate ions from solutions at pH 8 was achieved by synthesising layered zinc hydroxide nitrate (ZnHN) and zinc/indium layered double hydroxide salts (de Oliveira & Wypych, 2016). iii) In apolar organic solvents, layered zinc hydroxides coordinated by oleate ligands produce high-concentration solutions of isolated monolayers (Leung et al., 2018). LZH are a promising class of materials with potential applications in various industries such as environmental remediation, energy storage, and catalysis.

Apart from this, exfoliating LDH and LZH into single or few-layer nanosheets has many benefits, including greater surface area, enhanced properties, improved dispersion and a broad range of applications. These benefits make exfoliated LDH and LZH nanosheets highly appealing for various scientific and technological endeavours. There are several methods for the exfoliation of LDH and LZH such as top-down exfoliation, bottom-up direct synthesis, liquid phase exfoliation, and ultrasonic treatment.

Despite various exfoliation methods for LDH and LZH, choosing an appropriate solvent and exfoliating agent are key steps in exfoliating layered materials. Sugar molecules can be a great exfoliating agent due to their availability, renewable, and non-toxic carbohydrates (Aisawa et al., 2003). It contains a large number of hydroxyl groups which may greatly facilitate the exfoliation of layered materials. In addition, due to its higher dielectric constant, DMSO can be an excellent solvent, providing a higher solubility. DMSO is also miscible with water and most organic liquids (MacGregor, 1967). DMSO is less toxic than other organic solvents (Verheijen et al., 2019). Besides, water is non-toxic, abundant, and inexpensive compared to many organic solvents. Water can dissolve a wide range of polar and ionic compounds, making it useful for exfoliating various layered materials. Water also has a high dielectric constant, which reduces the attractive forces between ions in solution, allowing them to dissociate more easily (Lajoie et al., 2022).

Herein, the main study is to develop a facile method for the liquid phase exfoliation of layered metal hydroxides. Sugar molecules were used to exfoliate LDHs and LZHs in DMSO and water. In our studies, 1g sucrose, 1g glucose, 1g lactose, and 2g sucrose have been used but sucrose was used as the main exfoliating agent. Three different synthetic approaches have been carried out such as co-precipitation, reconstruction, and hydrothermal. Each synthetic method has its own advantages. For example, co-precipitation is a simple, effective method and can be easily scaled up. Reconstruction methods result in high purity materials while hydrothermal synthesis work in mild reaction conditions.

1.2 Problem Statements

Liquid phase exfoliation (LPE) using organic solvents is a widely adopted technique for obtaining thin, individual layers of various layered materials, including layered double hydroxide (LDH) and layered zinc hydroxide (LZH). Organic solvents, with their tunable properties, hold promise as an alternative approach for the

exfoliation of layered materials. However, despite their potential advantages, the exfoliation of layered materials using organic solvents present several unresolved issues and challenges that hinder its widespread adoption. The health risks associated with organic solvents in the exfoliation of layered materials are significant. These solvents present severe health risks, and in 2008, NMP and DMF were classified as Substances of Very High Concern. According to the European REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) regulation, several restrictions were applied regarding their use and import to Europe (Fernandes et al., 2022). The use of such solvents can impact the biological interactions and final biodistribution of material (Guiney et al., 2018). Organic solvents can be carcinogens, reproductive hazards, and neurotoxins. If inhaled or absorbed through the skin, solvents can cause breathing problems or rashes, and may lead to temporary nervous system symptoms, such as headaches, dizziness, numbness, and confusion (Rim, 2017). One example is formamide, a toxic and carcinogenic solvent that poses significant health risks. It is classified as a Class 1 solvent, which should be avoided in the production of drug substances, dietary supplements, and pharmaceutical drug products (Umamaheswari et al., 2021). Besides, organic solvents like acetone exposure can cause central nervous system effects, including headache and dizziness. It is also considered a volatile organic compound (VOT) and can contribute to air pollution if not handled and disposed properly (Dick, 2006). Therefore, it is essential to use less toxic and more sustainable solvents to minimize the impact on the environment and human health. Herein, we report the use of DMSO and water as a solvent for the exfoliation of layered materials using sugar molecules as exfoliating agent because it is considered safe and has a low toxicity profile. DMSO has low

acute and chronic toxicity for animal, plant, and aquatic life. DMSO is not listed as a

carcinogen by regulatory authorities and was placed in the safest category, class 3 solvents, with low toxic potential (Verheijen et al., 2019).

Furthermore, the reports on structural studies have been reported by Joensen et al. on XRD study on single-layer and restacked MoS2 (Joensen et al., 1986). The structural studies of a single layer of MoS2 in aqueous suspension show that a single layer differs from a bulk single crystal. When single-layer MoS2 suspension dries up, a new phase is obtained, whereas in dry restacked MoS2, bulk Mo-Mo distance starts to reappear. Sasaki et al. reported a stable colloidal suspension of an exfoliated titanate and the ensuing reassembling process (Sasaki et al., 1996). The layered protonic titanate was successfully exfoliated into single-layer nanosheets and the delaminated nanosheets were restacked upon drying; this reassembling process revealed the macromolecule aspects for the obtained individual nanosheets. XRD data showed that the amorphous halo changed into well order crystalline pattern upon drying. However, to our best knowledge, the structural information of LDH nanosheets in different sample phases using the X-ray diffraction (XRD) technique has never been reported. The study demonstrates for the first time the crystalline phase of LDH in different stages of liquid exfoliation; suspension, semi-dry suspension, and dried solid samples. We utilize different stages of liquid exfoliation to optimize the physical form, stability, and properties of exfoliated nanomaterials to enable their successful application in various fields in the near future.

1.3 Research Objectives

The objectives of this research are as follows:

- To exfoliate layered double hydroxides (LDHs) and layered zinc hydroxides (LZHs) using an exfoliating agent (sugar molecules) in dimethyl sulphoxide (DMSO) and ultrapure water.
- To determine the crystalline phase of LDH in different stages of liquid exfoliation; suspension, semi-dry suspension, and dried solid samples by Xray diffraction (XRD).
- iii. To characterise exfoliated layered double hydroxide (LDH) and layered zinc hydroxides (LZH) nanosheets using Fourier-transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), Brunauer-Emmett-Teller (BET) and transmission electron microscopy (TEM).

1.4 Scope of studies

This study uses the sugar molecules in DMSO and ultrapure water to exfoliate the layered double hydroxides (LDH) and layered zinc hydroxides (LZH). The research is limited to 1g sucrose, 1g glucose, 1g lactose and 2g sucrose. Sucrose is used as the main exfoliating agent via three different synthetic approaches: coprecipitation, reconstruction, and hydrothermal. We used different parameters such as the grams of sugar and synthetic approach to find an optimum result for the exfoliation. Besides, the research is limited to using dimethyl sulphoxide (DMSO) and ultrapure water as solvents. DMSO and ultrapure water are used for exfoliation of LDHs while for exfoliation of LZHs only ultrapure water is used. The research was conducted at the School of Chemical Sciences, USM lab for 12 months. The formation of singlelayer nanosheets and successful exfoliation was confirmed by the 3analysis of X-ray diffraction Fourier-transform infrared (XRD), (FTIR) spectroscopy, thermogravimetric analysis (TGA), differential Scanning Calorimetry (DSC), Brunauer-Emmett-Teller (BET) and transmission electron microscopy (TEM). The present study also explored the different stages of LDH exfoliation such as suspension, semi-dry suspension, and solid samples through the X-ray diffraction (XRD) technique.

CHAPTER 2

LITERATURE REVIEW

2.1 Layered materials

Mayans were among the first to use layered clays for dye production since the early 5th century (Coleman et al., 2011). The study of layered materials has evolved from a general exploration to a more systematic and scientific approach over time. Layered materials refer to a class of solids with robust chemical bonds within their planes while displaying weak interlayer bonds known as van der Waals forces. The materials can undergo shearing in a parallel manner or expansion in a direction perpendicular to a plane (Coleman et al., 2011). In extreme limits, the processes above produce extremely thin sheets, reaching the scale of nanometres or even individual atoms that exhibit distinct characteristics compared to the bulk precursor. The process of creating thin sheets from layered precursors is commonly referred to as exfoliation or delamination (Antonyraj et al., 2012). The term "nanosheets" is commonly used to describe the sheets' thinness, with "nano" denoting their small thickness. In an ideal situation, these nanosheets would be made up of a single monolayer, but most of the time they look like flakes with a small number (<10) of monolayers stacked on top of each other (Muthuraman & Kaur, 2017).

Layered materials encompass a wide array of categories, hence facilitating their classification into various distinct families. The most basic examples include graphene, which consists of atomically thin, hexagonal sheets and hexagonal boron nitride (h-BN) (Geim & Novoselov, 2007; Novoselov et al., 2012). Transition metal dichalcogenides (TMDs), including MoS₂ and WSe₂, and metal halides like PbI₂ and

MgBr₂ exhibit remarkably similar structures (Wilson & Yoffe, 2006). These compounds are composed of a metal atom plane sandwiched between halide or chalcogen atoms (Q. H. Wang et al., 2012). Besides, layered metal oxides (like MnO₂, MoO₃, and LaNb₂O₇) and layered double hydroxides (LDHs) (like Mg₆Al₂(OH)₁₆) are a group of materials with many different structures (Ma & Sasaki, 2010). In the same way, stacked silicates or clays are minerals that come in many different types, such as montmorillonite or micas (Luckham & Rossi, 1999). Other interesting families include the layered III-VIs (such as InSe and GaS), layered V-VIs (such as Bi₂Te₃ and Sb₂Se₃), metal trichalcogenides, and metal trihalides (Hasan & Kane, 2010). Layered metal oxides come in a wide variety, each with unique electrical, electrochemical, and optical properties (Ma & Sasaki, 2010). These materials have been utilised in the fabrication of transistors, battery electrodes, and magneto-optical devices (Osada & Sasaki, 2009). Therefore, layered materials are intriguing and possibly helpful materials even when present as bulk crystals. Because of this, they are a promising raw material for nanosheet exfoliation.

2.2 Layered double hydroxides (LDH)

The discovery of hydrotalcite in Sweden during the mid-19th century marks the beginning of the history of LDHs (Hasan & Kane, 2010). In 1915, Manasse introduced the precise formula, [Mg₆Al₂(OH)₁₆](CO₃).4H₂O, for the compound. The publication of a series of papers by Feitknecht has prompted the extensive investigation of LDHs (A. I. Khan & O'Hare, 2002a). Layered double hydroxide (LDH), commonly known as anionic clay or hydrotalcite-like materials. LDH are a broad family of 2D materials consisting of positively charged sheets of hydroxides intercalated by negatively charged anions (Bini & Monteforte, 2018). The structure of LDHs consists of layers of positively charged brucite-like material hydroxides, accompanied by charge-

balancing anions and water molecules inside the interlayer region (Hasan & Kane, 2010). Layered structure in these compounds enables the accommodation of various species between the layers. Besides, the anion exchange capacity value (AEC) of layered double hydroxide (LDH) varies between 200 and 400 meq/100 g, which surpasses the corresponding values observed in other clay minerals. This characteristic gives rise to a wide range of applications, including but not limited to their use as absorbents (Todorova et al., 2011), catalysts and catalyst precursors (Sandi, 2005), drug carriers (Hu et al., 2007), anion exchangers, and bioactive nanocomposites (Heraldy et al., 2016).

2.2.1 Structure of layered double hydroxides

According to the findings of Allmann et al., Brown et al., and Taylor et al., the structure of LDH was confirmed in the 1960s by means of single crystal X-ray diffraction research conducted on mineral samples (A. I. Khan & O'Hare, 2002a). The LDH structure has a strong resemblance to brucite, specifically Mg(OH)₂. It is characterised by the presence of neutral layers composed of edge-sharing Mg(OH)₆ octahedral units. These octahedral units are arranged in a hexagonal CdI₂ structure and are interconnected through hydrogen bonding interactions (Mills et al., 2012). The chemical formula commonly used to represent layered double hydroxides (LDH) is $[M^{z+}_{1-x}M'^{y+}_x(OH)_2]^{a+}(X^{n-})_{a/n}.bH_2O$. In this formula, M and M' represent metal cations with a charge of z = 1 or 2 and y = 3 or 4, respectively. The variable x represents the molar ratio of $M^{z+}/(M^{z+} + M'^{y+})$, 0 < x < 1 (C. Chen et al., 2014). Partially replacing M^{z+} ions with M'^{y+} gives the mixed metal hydroxide layers a net positive charge (a = z(1-x) + xy-2), which is balanced by the anions that build up in the interlayer region (X^{n-} , where n is between 1 and 3) (Costa et al., 2007). The layer gallery also consists of water molecules that undergo electrostatic interactions and form hydrogen

bonds with hydroxyl groups in the metal hydroxide layer and the interlayer anions, providing stability to the layered structure (M. Chen et al., 2016). The quantity of water molecules (b = 0-10), which includes both structural and physically adsorbed water, depends on the synthesis parameters (anion and reaction temperature) (C. Chen et al., 2014; Khan & O'Hare, 2002).

The LDH family is typically composed of divalent and trivalent metal cations. Divalent cations commonly found in LDH include Ca^{2+} , Mg^{2+} , Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , or Zn^{2+} . Trivalent cations that have been found identified in LDHs include Al^{3+} , Cr^{3+} , Mn^{3+} , Fe^{3+} , Co^{3+} , Ni^{3+} , or Ga^{3+} . The monovalent cation Li+ has been reported as the only component used in the preparation of layered double hydroxides (LDH), specifically [LiAl₂(OH)₇]·2H₂O (Meenakshi et al., 2019). In this process, an increase of Al^{3+} ions balances the additional positive charge. LD can also be synthesised using tetravalent cations such as Zr^{4+} and Sn^{4+} (Forano et al., 2006). Figure 2.1 shows a schematic representation of the prototypical carbonate LDHs.



Figure 2.1. Schematic representation of a typical MgAl-CO3-LDH structure (Salomão et al., 2011)

LDH are polymorphic, with two different configurations, hexagonal (2H) and rhombohedral (3R) (E. Zhitova et al., 2018). In the context of the arrangement of hydroxide ions in layers A, B, and C, the positioning of the metal and anion can be denoted by the variables m and x. The hexagonal stacking sequence can be described as a repeating pattern of AmB x BmA x AmB x..., as illustrated in Figure 2.2 (a). On the other hand, the rhombohedral sequence follows the pattern AmB x BmC x CmA x..., as shown in Figure 2.2 (b). In the rhombohedral and hexagonal forms of the crystal structure, the value of the lattice parameter c equals two and three times the interlayer distance (A. I. Khan & O'Hare, 2002b). While most naturally occurring LDH have rhombohedral symmetry, certain LDH possess a combination of both symmetry types. An example of such an LDH is pyroaurite $[Mg_6Fe_2(OH)_6](CO3)\cdot 4H2O$, which occurs naturally (E. S. Zhitova et al., 2023).



Figure 2.2. Schematic structure of LDH with (a) hexagonal (2H)110 and (b) rhombohedral (3R)109 packing sequences. Blue lines indicate the unit cell; A, B, and C present the hydroxide packing sequence relative to the c-axis, anions and water molecules are omitted for clarity (Ruengkajorn, 2017).

2.2.2 Unique properties of layered double hydroxides

LDH exhibit unique properties such as it has an excellent anion exchange capacity. It enables the reversible exchange of the interlayer anions with other anions in the solution (Pizzoferrato & Richetta, 2020). This property enables the combination of various anions, which can be modified for specific applications. Besides, LDHs have flexible compositions because they have guest anions in the interlayer and tunable metal cations in the host layer (C. Li et al., 2022). Modifying metal cations and anions can modulate the physicochemical characteristics of LDHs. LDHs typically have good thermal stability and can withstand high temperatures without losing structural integrity (Velasco et al., 2012). This feature is helpful for applications involving hightemperature processes. In addition, LDHs can store and release ions, making them suitable candidates for use in energy storage systems like batteries and supercapacitors (Matusik, 2021). It also can be used in environmental applications such as water treatment and pollutant removal (Zhai et al., 2022). Figure 2.3 below shows the unique properties of LDH.



Figure 2.3. Unique properties of LDH

2.3 Layered zinc hydroxides (LZH)

Layered zinc hydroxides (LZH) are classified as an inorganic layered material, having a layer structure that has a resemblance to brucite (Mg(OH)₂) and is also associated with anionic clay (Megat Nabil Mohsin et al., 2013). Layered zinc hydroxides (LZH) belong to the family of layered single metal hydroxides (LSHs). They are commonly represented by the chemical formula $Zn_5(OH)_8(NO_3)_2.2H_2O$, where A represents an intercalated anion such as carbonate, hydroxyl nitrate, carboxylate, or sulfate (Almasri et al., 2021). It has edge-sharing sheets of octahedral zinc hydroxide units where two tetrahedrally connected zinc ions are positioned above and below unoccupied octahedral sites (Gordeeva et al., 2020). Anions found in the interlayer space will even out the layer charge. LZH are appealing due to their easy synthesis process and high anion-exchange capacity (Ishikawa et al., 2006). There is a possibility to form double hydroxide salts [(Zn₂)(OH)₈(Aⁿ⁻)_{2/n}]·mH₂ by mixing Zn atoms with other metals, where M atoms (Ni or Co) are placed in octahedral locations

and Zn atoms placed in tetrahedral sites. In this aspect, Zn-hydroxide lamellae serve as desirable nano-building blocks for producing zinc oxide nanosheets (Demel et al., 2011).

2.3.1 Structure of layered zinc hydroxides (LZH)

The general layered structure displayed in Figure 2.4 is composed of zinc hydroxide layers comprising zinc ions that are octahedrally and tetrahedrally coordinated. The fundamental nature of LZH is characterized by a brucite-type structure, wherein a quarter of the zinc ion sites with octahedral coordination are unoccupied. The zinc (Zn) atoms are bound in a tetrahedral arrangement to the layer via hydroxyl (OH) groups, providing the foundation of a tetrahedron (Nabipour & Sadr, 2015). Additionally, the coordinated water molecules were situated at the apex of the tetrahedrons, while the nitrate groups were found in the interlayer area of LZH (Nabipour & Sadr, 2015). The nitrate anions are encompassed by water molecules, which are not directly coordinated with zinc atoms (Almasri et al., 2021). The lamellar structure exhibits a positive charge, resulting in the intercalation of counter anions and water molecules within the lamellar space to balance out the charge of the layers (Y. Zhang et al., 2021).

In contrast to LDH, the removal of hydroxide ions from the structure occurs through means other than metal replacement. Instead, these hydroxide ions are substituted by water molecules or other types of oxoanions, forming materials with anionic exchange capability (Gama et al., 2022). Moreover, water molecules have the potential to be incorporated into the interlayer region, resulting in increased stability (Theiss et al., 2014). The oxoanions are located within the metal's second coordination sphere to stabilise the electrostatic charge or can be directly substituted by another anion with a single charge (Machovsky et al., 2013).



Figure 2.4. Schematic representation of LZH structure (Gordeeva et al., 2020)

2.3.2 Unique properties of LZH

The unique properties of layered zinc hydroxide are its ability to undergo intercalation and exfoliation, which allows for incorporating various guest molecules or ions between its layers (Marangoni et al., 2009). This property makes LZH versatile in applications such as catalysis, energy storage, and environmental remediation (Abdallah et al., 2023). Furthermore, the layered structure of LZH provides a platform for easy modification and functionalization, enabling the development of tailored materials with specific properties for specific applications (Demel et al., 2014). Besides, LZH has a high surface-to-volume ratio, enhancing its reactivity and adsorption capacity (Soltani et al., 2017). This makes LZH highly efficient in capturing and removing pollutants from air or water, making them ideal for environmental remediation (de Oliveira & Wypych, 2016). The high surface-to- volume ratio also facilitates efficient charge transfer and ion diffusion, making LZH

promising candidates for energy storage devices such as batteries and supercapacitors (X. Li et al., 2023). In LZH, the exchangeable anion is crucial in determining their properties and applications. By selecting different exchangeable anions, the properties of LZH can be tailored to suit specific needs (Liu et al., 2019). The ability to easily exchange the anion in LZHs allows for versatility and adaptability in various fields.

2.4 Exfoliation in layered materials

The groundbreaking finding in 2004 by Novoselov and Geim regarding the existence of single-layer graphene proved the possibility of exfoliating stable, twodimensional (2D) materials with a single atom thickness from van der Waals solids. These 2D materials have unique properties, such as high carrier mobility at room temperature, the quantum hall effect, a large theoretical specific surface area, and outstanding optical transparency (Butler et al., 2013; Novoselov et al., 2004). The remarkable discovery made by Novoselov and Geim in 2010 led to their successful nomination and subsequent awarding of the Nobel Prize. The remarkable achievements of graphene have drawn significant attention and interest worldwide towards the exploration and study of two-dimensional (2D) materials. The ideal 2D materials are characterized by having a thickness of either one atom or a few atoms and having an infinite lateral size. The exfoliation of single and few-layer 2D materials is a significant first step in understanding the layer-dependent variations in their properties and facilitating their incorporation into various applications (Jianghao Wang et al., 2016). The development of exfoliation methods for layered materials has attracted considerable interest due to the intriguing properties and vast application potential of two-dimensional nanosheets in numerous areas. Figure 2.5 below shows the numerous exfoliation techniques used for layered materials.



Figure 2.5. Exfoliation in layered materials

2.4.1 Ultrasonic exfoliation

Ultrasonication has been extensively employed as a method to assist in the exfoliation process of layered structures (Coleman, 2013; Haar et al., 2016; Parvez et al., 2014). Ultrasound waves consist of compression and rarefaction cycles. Cavitation is a phenomenon that occurs during the rarefaction cycles, where the application of acoustic pressure leads to the formation of stable or transient microbubbles, also known as cavities. Transient cavitation is a phenomenon in which bubbles grow via rectified diffusion and coalescence. Upon reaching a critical size, it has been observed that the bubbles undergo a sudden collapse with an instantaneous temperature of up to 5000 K, local pressure reaching 20 MPa, and a heating/cooling rate of up to 10^9 K/s (Hayashi et al., 2022). Consequently, the formation of shock waves occurs, potentially breaking large flakes into thinner layers. Furthermore, microturbulence (also known as micro-convection) and pitting effects, which arise from the collapse of bubbles,

provide mechanical energy mainly in the form of tensile stress. This energy prevents attractive interactions between the layers, ultimately leading to exfoliation. Simultaneously, the fragmentation process, namely the flake cutting, may occur near cavitation bubbles. This phenomenon can be due to the frictional force arising from the high strain rates, reaching up to 109 K/s (Montagna et al., 2017). Edge defects are observed to be induced as a result of prolonged exposure to ultrasonic irradiation. This leads to an increase in surface polarity, thereby enhancing the dispersibility of the material.

Research conducted by Kim et al. has confirmed that the functionalization of h-BN and MoS₂ nanosheets does not occur even with ultrasound treatment at elevated temperatures of 60 °C (Kim et al., 2015). Nevertheless, when graphene is subjected to an ultrasonic bath at temperatures over 40 °C, carbon atoms that are positioned at the edges of the material have a tendency to react with radicals or ions that arise from the dissolution of water during the process of cavitation (Kim et al., 2015). Consequently, the introduction of hydroxyl, carboxyl, or epoxy groups occurred in graphene. The above findings align with previous studies that have demonstrated the formation of oxygenated species in the lattice of exfoliated graphene as a result of the interaction with air during ultrasonication (Skaltsas et al., 2013; Bracamonte et al., 2014). Despite the introduction of defects caused by ultrasonic, the domain size of exfoliated graphene remains rather big, reaching around 14,600 carbon atoms. This size is notably greater than that reported in chemically produced graphene, which typically consists of approximately 9,900 carbon atoms (Xu et al., 2018).

In a recent study conducted by Zecchina et al., it was discovered that applying MoS₂ to intensive ultrasonication in isopropyl alcohol (IPA) resulted in favorable exfoliation. Additionally, this process induced fragmentation of the layers, causing the

rupture of Mo-S-Mo bonds and exposing coordinatively unsaturated Mo and S species. The ultrasonication parameters used in the experiment were 20 kHz frequency, 500 W power, a probe diameter of 3 mm, and 30% amplitude. These species can undergo reactions with the IPA solvent or air oxygen, resulting in the formation of surface hydroxyl, alkyl, and to a lesser extent, oxidized species such as sulfate, carbonylic, and carboxylate groups (Muscuso et al., 2015).

With ultrasonic exfoliation, you can get dispersions of volumes that are usually in the hundreds of millilitres range (U. Khan et al., 2010). Depending on the starting material, the nanosheets made are a few layers thick and range in width from 50 nm to 2 m. More exfoliated nanosheets can be made when an intense ultrasonic probe is used instead of a mild ultrasonic bath (Arao & Kubouchi, 2015) and the ultrasonic time is increased (Lotya et al., 2010). In fact, Khan et al. found that the graphene concentration (C_G) increased with ultrasonic time (t) as shown by $C_G \propto t^{1/2}$ (U. Khan et al., 2010). However, flake dimensions decreased with ultrasonic time, possibly as much as $t^{-1/2}$, and several new defects were introduced with prolonged ultrasonication. Even after 4 hours of ultrasonication in a PEGPPGPEG Pluronic aqueous solution, the formation of WS₂ nanodots was observed (X. Zhao et al., 2016). Lee et al. demonstrated the highly effective exfoliation of TMD nanosheets in dimethyl sulphoxide (DMSO) and N-methyl pyrrolidone (NMP) by combining ultrasonic cavitation and microbubble formation by aeration (Han et al., 2014). This process is said to cause minimal nanosheet cutting and defect development without solvent molecule sonolysis. Hao et al. solved the "Magdeburger Halbkugeln" issue in ultrasound by combining ultrasonication with magnetic stirring, resulting in 95% apparent yields for graphene, h-BN, MoS₂, and WS₂ exfoliation in aqueous solutions (G. Zhao et al., 2016). However this ultrsound treatment can cause damage to the material being exfoliated

due to their high energy ultrasonic wave. This high energy ultrasonic wave may cause defects and impurities in the resulting material.

According to Nagendra, the sonication-assisted delamination of layered double hydroxides (LDHs) produced LDH nanoparticles of reduced size (50-200 nm) (Nagendra et al., 2017). These delaminated CoAl LDH, ZnAl LDH, and CoZnAl LDH solutions produce highly dispersed isotactic polypropylene (iPP) nanocomposites. The results of transmission electron microscopy and wide-angle X-ray diffraction showed that the LDH nanoparticles were evenly distributed throughout the iPP matrix. The nanocomposites prepared with three-metal LDH exhibited superior thermal and flameretardant properties compared to those prepared with two-metal LDH. On the other hand, an easy and green method for improving the oxygen evolution activity of NiFe LDH supported on carbon black (CB) has been presented by Munonde et al. (Munonde et al., 2019). To increase the activity of NiFe LDH/CB towards OER, ultrasonic exfoliation 20 kHz, 500 W) has been used specifically with an overpotential of 220 mV at a current density of 10 mA cm², which is 60 mV lower than the 280 mV of the bulk NiFe LDH/CB. The exfoliated NiFe LDH/CB nanosheets exhibit much stronger OER activity than their equivalent bulk NiFe LDH/CB in an alkaline solution.

Recently, Telkhozhayeva et al. reported that higher ultrasonic frequency liquid phase exfoliation leads to larger and monolayer to few-layer flakes of 2D materials. The monolayer graphenes were directly exfoliated from graphite using ethanol as solvent by increasing the frequency of bath sonification. The statistical analysis revealed the yield of monolayers at 80 kHz bath sonication to be 31.6%, 43.3%, and 50% for graphene flakes, Cu₉S₅ flakes, and Ag₂S flakes, respectively (Telkhozhayeva et al., 2021). Although this method produces monolayers and a few layers of highquality graphene, there are still some drawbacks. One of the challenges might be higher energy consumption, ultrasonic exfoliation can cause significant amount of energy, which can make the exfoliation process expensive. The high frequency and power of ultrasonic waves can affect the thickness and size of flakes.

Layered materials	Exfoliation conditions	Exfoliation State	Reference
Graphene	Ultrasoncic bath at 40°C	Successful	Kim et al., 2015
MoS ₂	Intensive ultrasonification in isopropyl alcohol (IPA), 20 kHz, 500 W	Successful	Muscuso et al., 2015
WS ₂	Ultrasonification in a PEGPPGPEG, pluronic aqueous solution	Successful	X.Zhao et al., 2016
TMD	Ultrasonic cavitation in DMSO and NMP	Successful	Han et al., 2014
Graphene, h-BN, MoS ₂ , and WS ₂	Ultrasonic with magnetic stirrring	Successful	G.Zhao et al., 2016
Co/Al-LDH, Zn/Al-LDH, CoZnAl-LDH	Sonification-assisted delamination	Successful	Nagendra al., 2017
Ni/Fe-LDH	Ultrasonic exfoliation (200 kHz, 500 W)	Successful	Munonde et al., 2019
Graphene, digenite, silver sulfide	Ultrasonic bath at 80 kHz	Successful	Thelkozhayeva et al., 2021

Table 2.1: Comparison of ultrasonic exfoliation in layered materials