

**Development of
Hybrid
Layered Double Hydroxide Nanomaterials**

by

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ABSTRACT

Nanotechnology which brings colloidal science, physics, chemistry, biology and engineering together to design, create, fabricate and utilize functional structures lies among the state-of-the-art technologies of the modern world. The high accreditation of nanotechnology stems from the fact that the physical and chemical properties of materials differ significantly from their bulk counterparts when they are below 100 nm scale and exhibit intermediate features reside between isolated atoms and bulk materials. This special feature opens out an exciting field for new scientific advancements.

Layered double hydroxides (LDHs) are a class of anionic clays where the metal layers are positively charged and the charge balance is provided by the interlayer exchangeable anions. The chemical composition of LDHs is generally expressed with the $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}(A^{n-})_{x/n} \cdot yH_2O$ formula where M^{II} and M^{III} represent divalent and trivalent metal cations, respectively, and A^{n-} represent the interlayer anion. LDHs are one of the most useful inorganic layered materials since the identity of the M^{II} and M^{III} cations and the guest anion in the interlayer can be varied in a wide range constituting a very large family of materials which can be used in electrochemistry, and cosmetics, or as catalysts, as adsorbents, as fillers or stabilizers in polymer blends, as well as flame retardants, drug stabilizers and drug/gene carriers. Since often shape and size dictates the properties and applications, there is a great interest in obtaining advanced materials with altered morphologies. Recently, the template-assisted synthesis of the layered double hydroxides with surfactants has gained interest. In this study, the influence of the surfactant type sodium dodecyl sulfate (SDS) and sodium laurate (SL) and concentration as well as the reaction time on the Zn-Al LDH morphology synthesized via urea hydrolysis method was investigated. To the best of our knowledge, hollow ring morphology for SDS intercalated Zn-Al LDH was observed for the first time in the literature under the conditions where the amount of the SDS is 20 times higher than the stoichiometric ratio needed for the charge balance. This phenomenon is strictly

surfactant-type dependent. The same concentration of SL yielded in the formation of rod-like zinc hydroxide intercalated with surfactant, which is also new in the literature.

Applications of LDHs in the medical field lack an important characteristic: we are unable to detect LDHs inside body in medical applications. Therefore, part of this thesis is devoted to the development of quantum dot intercalated LDH, which utilizes the biocompatibility and transport properties of LDHs and the optical properties, namely the luminescence, of quantum dots, simultaneously. Different preparation methods and the influence of LDH on the properties of quantum dots, specifically size, luminescence and stability, were investigated. Luminescent LDH/QD hybrids were produced. This LDH/QD hybrid promises a high potential in the pharmaceutical and biological applications.

ÖZET

Kolloid bilimini, fizik, kimya, biyoloji ve mühendisliği fonksiyonel yapılar tasarımı yapmak, yaratmak ve üretmek için bir araya getiren nanoteknoloji modern dünyamızın en gelişkin teknolojilerinin arasındadır. Nanoteknolojiye duyulan yüksek ilginin nedeni 1-100 nm boyutundaki malzemelerin daha büyük boyuttaki parçacıklara göre fiziksel ve kimyasal özelliklerinin önemli farklar göstermesinde ve izole atomlarla büyük parçacıklar arasında olmasında yatmaktadır. Bu özellikler pek çok yeni bilimsel gelişmelere kapı açmaktadır.

Anyonik killeri sınıfının bir üyesi olan katmanlı çift hidroksitler (KÇH), pozitif yüklü metal tabakaların ve katmanlar arasında yük dengesini sağlayan, yer değiştirebilen anyonların oluşturduğu yapılardır. KÇHlerin kimyasal yapısı; M^{II} ile M^{III} 'ün sırayla brüsit katmanları oluşturan iki ve üç değerlikli katyonları, A^{n-} 'in ise iç tabakadaki anyonu temsil ettiği $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}(A^{n-})_{x/n} \cdot yH_2O$ formülü ile gösterilir. X' katsayısı ile katyon ve anyonların geniş bir aralıkta değiştirilerek geniş bir aile oluşturmaları nedeniyle elektrokimya, kozmetik, kataliz ve tıp gibi birçok alanda kullanılabilen KÇHler en yararlı anorganik katmanlı malzemeler arasındadır. Genellikle boyut ve biçim malzemelerin özelliklerini ve uygulama alanlarını belirlediğinden, değişik morfolojilerde, gelişmiş malzemeler hazırlamak büyük ilgi duyulan bir alan haline gelmiştir. Yakın zamanda, KÇHlerin çeşitli kalıplarla sentezi önem kazanmıştır. Bu çalışmada yüzey-aktif madde tipi ve konsantrasyonun üre-hidrolyzisi metoduyla hazırlanmış Zn-Al KÇH morfolojisi üzerindeki etkileri araştırılmıştır. Sodyum dodesil sülfat (SDS) ve laurik asit sodyum tuzu (SL) olmak üzere iki farklı yüzey aktif maddeyle çalışılmıştır. SDS ilave edilmiş Zn-Al KÇH için, yüzey-aktif-madde miktarının yük dengesi için gerekenden 20 kat fazla kullanılmasıyla elde edilen içi boş halka morfolojisi literatürde ilk kez gözlenmiştir. Bu etkinin kesinlikle yüzey-aktif-madde tipine bağlı olduğu görülmüştür. Aynı konsantrasyonda sodyum laurik asit sodyum tuzu (SL) ilave edilmesi çubuk benzeri morfolojiye sahip çinko hidroksit oluşumuna neden olmuştur ki bu da literatürde yenidir.

KÇHler tıbbi alandaki uygulamalarda önemli bir eksiklik göstermektedirler: KÇHlerin vücut içinde tespiti zordur. Bu yüzden, bu tez çalışmasının bir kısmı da kuantum noktacıkları (KN) ilave edilmiş KÇH geliştirmeye adanmıştır. KÇH/KN hibridleri KÇHlerin biyo-uyumluluk ve ilaç taşıma özellikleriyle KNların ışıma özelliğinin bir arada kullanılmasını mümkün kılacaktır. Farklı hibrid hazırlama metodlarıyla; KÇHlerin KNların boyut, ışıma ve kararlılıkları üzerindeki etkileri incelenmiştir. KÇH/KN hibridleri farmasötik ve biyolojik uygulamalarda yüksek potansiyel vaad eden, ışıyan KÇH/KN hibridleri üretilmiştir.

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NOMENCLATURE

<i>QD</i>	quantum dot
<i>QY</i>	quantum yield
<i>STM</i>	scanning tunneling microscope
<i>DMSA</i>	meso-2,3-dimercaptosuccinic acid
<i>3-MPA</i>	3-mercaptopropionic acid
<i>2-MPA</i>	2-mercaptopropionic acid
<i>TAA</i>	thioacetamide
<i>TOP</i>	trioctylphosphine
<i>TOPO</i>	trioctylphosphineoxide
<i>DOS</i>	density of states
<i>LED</i>	light emitting diode
<i>UV</i>	ultraviolet
<i>IR</i>	infrared
<i>UV-Vis</i>	ultraviolet-visible
<i>PL</i>	photoluminescence
<i>FTIR</i>	fourier transform infrared
<i>XRD</i>	powder x-ray diffraction
<i>-COOH</i>	carboxylic acid group
<i>-SH</i>	thiol group
<i>E_g</i>	band gap energy
<i>E_C</i>	conduction band energy
<i>E_v</i>	valance band energy
<i>E_k</i>	kinetic energy of carriers
<i>E_{Coul}</i>	coulomb energy
<i>h</i>	Planck's constant

r	average radius of quantum dots
d	average diameter of quantum dots
μ	reduced mass of the exciton
m_e^*	effective mass of electron
m_h^*	effective mass of hole
m_e	mass of electron
e	electron charge
ε	dielectric constant
ε_0	vacuum permittivity (or electric constant)
c	speed of light
ν	frequency of electromagnetic radiation
λ	wavelength of electromagnetic radiation
A	optical density at the excitation wavelength average
n	refractive index of a solution
F	integrated area under the corrected emission spectrum
pH	potential hydronium ion concentration
nm	nanometer
μm	micrometer
<i>LDH</i>	layered double hydroxide
<i>CMP</i>	cytosine monophosphate
<i>AMP</i>	adenosine monophosphate
<i>GMP</i>	guanosine monophosphate
<i>DNA</i>	deoxyribonucleic acid
<i>EBR</i>	exciton Bohr Radius
<i>FWHM</i>	full width at Half Maximum
<i>HMT</i>	hexamethylenetetramine
<i>CMC</i>	critical micelle concentration
R_h	hydrodynamic radius

<i>SDS</i>	sodium doceyl sulfate
<i>SL</i>	sodium laurate
<i>ICP</i>	inductively coupled plasma
<i>TGA</i>	thermal gravimetric analysis
<i>d</i>	basal spacing
<i>AEC</i>	anion exchange capacity
<i>SEM</i>	scanning electon microscope
<i>PAA</i>	polyacrylic acid sodium salt

Chapter 1

INTRODUCTION

New technological advancements and new challenges are awaiting for scientists since Richard Feynman pointed out that ‘there is plenty of room at the bottom’ in a lecture at an American Physical Society meeting at Caltech on December 29, 1959. He envisioned manipulation of matter at the atomic scale is possible which is a loose definition of nanotechnology today and enlightened the path to the invention of scanning tunneling microscope, the atomic force microscope and other examples of probe microscopy that enables us to characterize materials at the nanoscale. However, official description of nanotechnology was made long after nobel laurate Feynman by Professor Norio Taniguchi as ‘processing, separation, consolidation, and deformation of materials with structural features in between atoms as well as bulk materials’.¹

Nanotechnology brings colloidal science, physics, chemistry, biology and engineering together to design, create, fabricate and utilize functional structures with at least one dimension in the nanoscale. The reason for high accreditation of nanoscience stems from the fact that the physical and chemical properties of materials differ significantly from their bulk counterparts when they are of 1 to 100 nm and exhibit intermediate features reside between isolated atoms and bulk materials. This features created an exciting field for new scientific advancements. One of the important features of nanomaterials is the high surface to volume ratio. As dimensions of the particles decrease the surface to volume ratio increases. This macroscopic change increases the reactivity of the nanoparticles compared to the bulk. For example, gold nanoparticles

need to be smaller than 8 nm in diameter to act as catalysts² in cleaning procedure of the exhaust gases. Pd nanoparticles are also more effective catalysts than commercial black Pd.³ The structural, magnetic⁴, thermal⁵, mechanical⁶, electrical⁷ and optical⁸ properties of materials change on reduction of the scale to nanometer range in line with quantum mechanical properties. Among such materials one of the most exciting one is quantum dots (QDs). With their unique electronic nature and optical properties, they arouse great interest in many fields such as microelectronics, nanobiotechnology, photovoltaics and optics.

Another fast growing research area is the field of nanocomposites. Nanocomposites bring two phases together one of which has at least one dimension smaller than 100 nm to create new materials with novel properties. The nanoparticles embedded in the host material enhance the magnetic, electrical, thermal and optical properties of the host. The host can be zeolites, two-dimensional layered materials such as clays, metal phosphates or metal hydroxides. Layered materials alone exhibit unique features that can be used in electronics, photoelectronics and catalysis. As much as the host layer properties, the interlayer galleries or nanospace between the layers attain great interest from both academia and industry. A new nanohybrid material can be formed by introducing new guest species in this nanospace.

The research summarized in this M.S. thesis is focused on developing layered double hydroxides (LDHs) with unique morphology and creation of new nanohybrid materials by introducing QDs as guest anions among layers of double metal hydroxides. The emphasis will be on the fundamental properties of LDHs and QDs in the following sections.

1.1 Layered Double Hydroxides

Layered double hydroxides (LDHs), a class of anionic (smectite) clays, where the metal layers are positively charged and the charge balance is provided by the interlayer, exchangeable anions. The chemical composition of LDHs is generally expressed with the $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}(A^{n-})_{x/n} \cdot yH_2O$ formula where M^{II} and M^{III} represent divalent and trivalent metal cations respectively, and A^{n-} represent the interlayer anion. They were first discovered in the 19th century when first natural hydrotalcite was found in Sweden in 1842.⁹ It was 1942 when the interest in LDHs has been increased after Feitknecht published papers where he assigned alternating layers of M^{II} and M^{III} cations for the structure.¹⁰ He was proved wrong later by Allman and Taylor who proposed the layered structure we are using today after single crystal X-ray crystallography analysis.⁹

1.1.2 Structure

The structure of LDH is based on naturally occurring mineral brucite ($Mg(OH)_2$). In a brucite layer Mg^{2+} cations are octahedrally coordinated with the hydroxyls.¹¹ These octahedra edge-share to form infinite layers with hydroxyl groups perpendicular to the layers, in the crystallographic a and b directions. These layers are stacked on top of each other and held together by H-bonds (Figure 1.1). In the actual structure, the octahedrons are compressed and the local geometry around the metal is distorted from O_h to D_{3d} .¹² In spite of the distortion, the brucite has still hexagonal symmetry with cell parameters $a_o = b_o = 0.3142$ nm, $c_o = 0.4766$ nm, $\gamma = 120^\circ$.

A LDH is constructed by the substitution of some of the M^{II} cations in brucite by M^{III} cations rendering the overall structure with positive charge. This extra charge is balanced by anions present in between the layers. The number of the anions that might

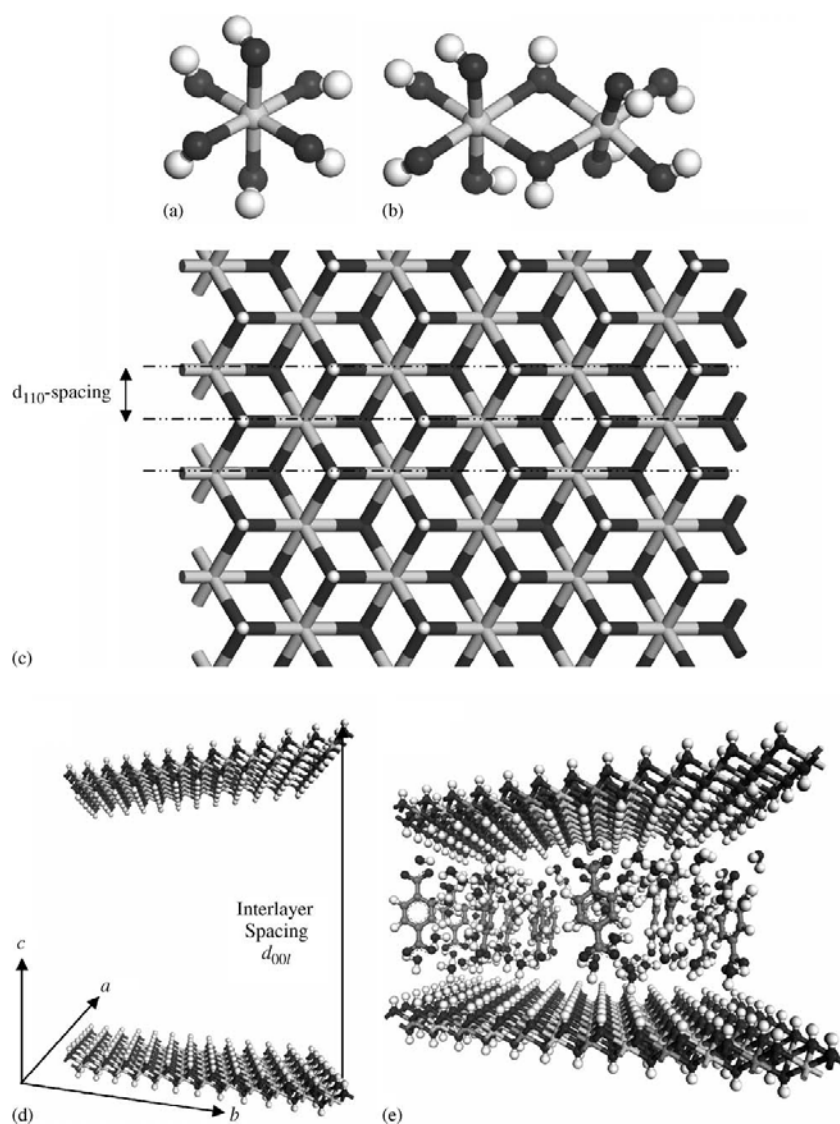


Figure 1.1 Structure of LDHs with reference to brucite ($\text{Mg}(\text{OH})_2$).¹¹ a) Octahedral coordination of Mg^{2+} cations (pale grey) with hydroxyls (O: dark grey, H: white). b) Edge sharing octahedra. c) 2-dimensional sheets formed by edge sharing octahedra. (d) These sheets stack to form a layered structure. (e) In MgAl LDHs Al^{3+} replaces some of the Mg^{2+} and the excess charge is balanced by anions (terephthalate is shown as interlayer anion).

be intercalated within the layers known as the anion exchange capacity (AEC) depends on this extra charge which is related to the amount of M^{III} . Water molecules also fill up the available sites in the galleries.¹³ The theoretical thickness of an LDH layer is 0.48 nm.¹⁴ The possibility of varying the identity of the divalent and trivalent cations as well as the interlayer anion gives rise to a large family of LDH. LDHs even with a mixture of different M^{II} and M^{III} cations (ternary and quaternary LDH), and with $M^I:Li^{1+}$ and $M^{III}:Al^{3+}$ have been prepared.^{10, 12} It has been argued that the identities of the metal cations are restricted by the similarity of the ionic radii to that of Mg^{2+} and the solubilities of $M(OH)_2$ and MCO_3 .¹⁰ Nevertheless LDHs with $M^{II} : Ca^{2+}, Mg^{2+}, Zn^{2+}, Ni^{2+}, Mn^{2+}, Co^{2+},$ or Fe^{2+} and with $M^{III} : Al^{3+}, Cr^{3+}, Mn^{3+}, Fe^{3+}, Ga^{3+}, Co^{3+}$ or Ni^{3+} have been reported.^{9, 10} It has been argued that x should be in between 0.20 and 0.33 to obtain pure LDH phases since a high value of x indicate M^{III} cations are closer which is not favorable due to charge repulsion and a low value of x might result in formation of $M(OH)_2$. However, LDHs with x values beyond the range around 0.07 and 0.5 has been reported for Mg-Ga – CO_3 LDHs and Fe^{II} - Fe^{III} LDHs, respectively.¹²

Stacking of the LDH layers with interlayer anions give rise to two polytypes of crystal lattices; rhombohedral and hexagonal (Figure 1.2). The rhombohedral unit cell consists of three repeating units (an octahedral layer and plus an interlayer) and the hexagonal unit cell consists of two repeating units.¹³ The difference between the two polytypes lies in the long-distance layer–layer interactions.

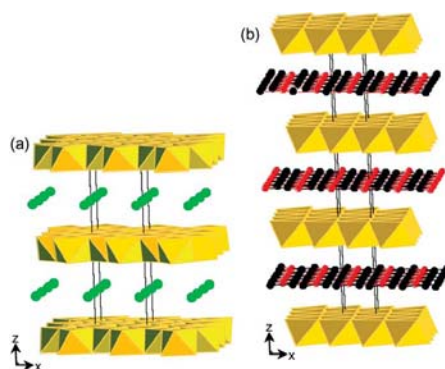
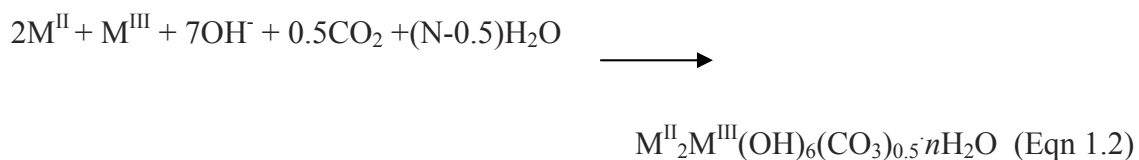
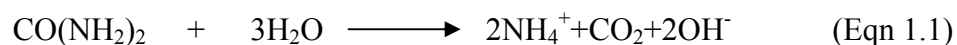


Figure 1.2 LDH with 2 different stacking patterns a) hexagonal b) rhombohedral¹⁰

1.1.3 Synthesis Methods

The most commonly used method for the preparation of LDHs is co-precipitation of the metal salts at high pH in aqueous solution of the desired anion.^{15, 16} The strength of this method lies in the fact that the particle properties such as size and morphology can be tailored by varying the reaction conditions such as concentration of the metal salt and the anion, pH, temperature, mixing rate. Co-precipitation can be achieved either at varying pH or constant pH. In the varying pH method, the mixed metal salts are added on a solution containing Na₂CO₃ until the pH reaches a specific value and then pH is kept constant until after the reaction is complete with NaOH. LDH-CO₃ is obtained at the end of the reaction.¹⁷ Constant pH method is applied at low supersaturation through dropwise addition of mixed metals salt solution and base solution into the reaction vessel at a rate that would keep the pH constant.¹⁷ The outstanding feature of this method is various LDHs constituting different guest anions can be prepared. LDHs bearing Cl⁻, CO₃²⁻, tartrate, succinate,¹⁸ folic acid¹⁹ and alginate²⁰ have been prepared with this route. Another technique is ‘urea hydrolysis or homogeneous precipitation method’. In this ‘homogenous precipitation method’, urea being a Bronsted base (pK_b = 13.8) undergoes hydrolysis and releases ammonia at elevated temperatures which causes an increase in the pH hence the precipitation of the LDHs together with CO₂ and OH⁻ (Eqn 1.1). This hydrolysis reaction yields highly crystalline CO₃²⁻ intercalated LDHs through coprecipitation of M²⁺ and M³⁺ to form the LDH crystal nucleus (Eqn 1.2).²¹



Other ammonia releasing agents rather than urea are also used for homogenous precipitation.²² This technique generally yields monodisperse, well crystallized LDH platelets.²³ Hydrothermal synthesis is also used to yield intercalated LDH which is not possible to obtain by other means such as metal oxalate complex-intercalated LDH²⁴ or deoxycolate-intercalated LDH.²⁵ In this method LDH is usually formed from metal oxide or metal hydroxide precursors which sustain an environment where only possible intercalation molecule is the desired anion.¹⁷ There are also indirect methods giving an opportunity to prepare LDHs with a wide range of guest anions which require a precursor material. First one is direct-ion exchange. In this method, the precursor LDH is re-dispersed in a solution of the desired anion and the exchange reaction of the interlayer anion in the precursor is preformed under inert atmosphere to avoid intercalation of CO_3^{2-} . The reaction pH, charge of the ‘incoming’ anion, exchange medium, and chemical composition of the layers affect the yield of the reaction.¹⁷ Generally LDHs bearing monovalent anions like Cl^- or NO_3^- are used as starting materials.²⁶ It is important that both the guest anion and the precursor LDH are stable in the reaction conditions. The second indirect method makes use of the *structural memory effect* upon rehydration. It is also known as *rehydration* or *reconstruction*. This method involves calcinations of the precursor LDH into layered double oxide (LDO) material and reconstruction of the mixed oxide in the presence of the desired anion in water.²⁶ Water forms the hydroxyl layers during the re-absorption and is intercalated together with the anions. This method is applied for the intercalation of large molecules.¹⁷ Furthermore, template synthesis using self-assembled aggregates to manipulate the morphology of the LDHs in accordance with the structure of the self-assembly is used. Peptides, polysaccharides, amphiphilic block polymers, Langmuir-Blodgett films, microemulsions, vesicles, and micelles consisting of surfactants are used as templates which will be discussed in detail in Chapter 2.¹⁷

1.1.4 Bio-Applications of LDHs

LDHs are one of the most useful inorganic layered materials since they can be used in electrochemistry²⁷, to create magnetic materials²⁸, in cosmetics²⁹, as catalysts³⁰, as adsorbents³¹, as fillers or stabilizers in polymer blends³², as flame retardants and improve mechanical properties of polymers³³, as drug stabilizers³⁴ and drug/gene carriers^{5, 35-38}. However, we are interested in the biological applications in this Ms. Thesis.

LDHs are preferred in pharmaceuticals and cosmetics not only to build novel hybrid systems but also to protect biomolecules mostly due to their acid buffering effect and anion exchange capacity.²⁹ Mostly Mg-Al LDH is used in this field, however the ZnO-Al₂O₃ formed from Zn-Al LDH is also shown to be bactericidal.³⁹ The strength of the LDHs in the medical field relies on the fact that a large variety of the biomolecules can be loaded and unloaded in the inter gallery through anion exchange. Choy et al. pioneered in the intercalation of biomolecules such as CMP (Cytidine monophosphate), AMP (Adenosine monophosphate), GMP (Guanosine monophosphate) and DNA.⁴⁰ The DNA-LDH hybrid was shown to be stable under acidic conditions and in the presence of DNase and it yielded the undamaged DNA in acidic conditions. This work was followed by many studies to intercalate antisense oligonucleotides^{41, 42}, long DNA fragments⁴³, supercoiled plasmid DNA⁴⁴ and many others proving the potential of LDH hybrids in the field of gene therapy to treat various cancers. Furthermore, M.J. Masarudin *et al.* actually showed successful transfer of the gene encoding for the green fluorescent protein into African monkey kidney cells.³⁷ One of the recent studies enhances the LDH nanoparticle towards targeted delivery demonstrating the site specific clathrin-mediated endocytosis of the particles.⁴⁵

Despite of this tremendous potential of LDH particles in medicine, there is a need to develop a system which will render LDHs suitable for tracking in vivo delivery kinetics, tumor biology investigation, and diagnostics. Choy *et al.* reported the use of

^{32}P to determine the uptake efficiency of adenosine 5'-triphosphate intercalated LDH nanohybrids.⁴⁶ The use of ^{32}P allows the tracking of the adenosine derivative but does

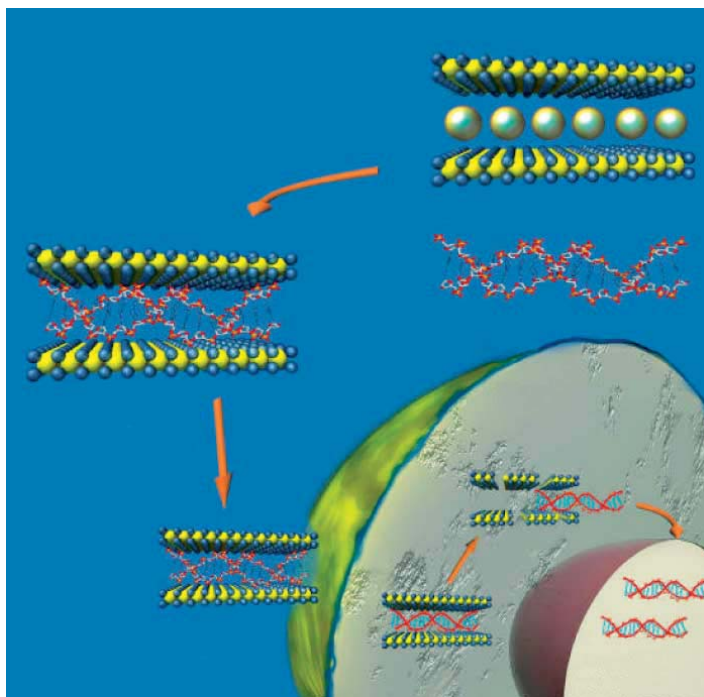


Figure 1.3 Illustration of the construction and transfer mechanism of the bio-LDH nanohybrid into a cell.⁴⁷

not track the fate of the LDH nanoparticles. They argued that LDH nanoparticles dissolve in the pH range 3-4. Another group used radiolabeling to track LDH particles and their dissolution behavior in different pH values.⁴⁸ These are the only studies that involve the tracing of the LDH nanohybrids to the best of our knowledge. Hence, there is still a need to develop safer and high-quality systems to understand the fate of these clay nanohybrids inside the cells.

1.2 Quantum Dots

Quantum dots (QD) are colloidal semiconductors of only a few nanometers in size that exhibit unique optical and electrostatic properties, which cannot be achieved

by micron scale particles. Almost 2000 QDs of 5 nm are needed to equate the diameter of a white blood cell and approximately 8000 to equate the thickness of an average human hair (Figure 1.) Semiconductor quantum dots are usually composed of II-VI (CdS, CdTe), III-V (GaAs, InP) or IV-VI (PbS, SnTe) group elements but behave significantly different at such small size regime. These unique properties result from quantum confinement which will be explained in detail in the next section.

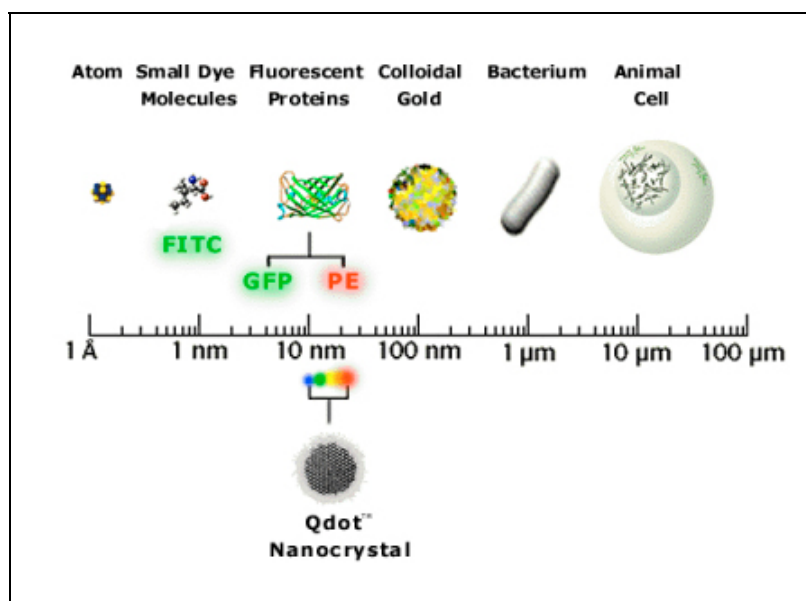


Figure 1.4 Size comparison of QDs (<http://www.nanotech-now.com>)

1.2.1 Quantum confinement and Optical Properties

For bulk materials energy levels are the solutions of the Schrödinger equation with the assumption of ‘particle-in-a-box’ where free valence electrons are constrained in a potential well. Then the set of electronic energy levels is represented by,

$$E_n = \frac{n^2 h^2}{8m^* L^2}, \text{ where } n=1, 2, 3, \dots, h \text{ is the Planck's constant, } m^* \text{ is the effective mass, } n \text{ is the principal quantum number and } L \text{ is the length of the one dimensional box.}$$

(Eqn 1.3)

The relationship between n and E_n is parabolic and the permitted energy levels on this parabola are discrete. However, since L is much smaller than thermal energy for most metals, the energy distribution is regarded as almost continuous.¹ The forbidden energy levels of a semiconductor metal create a narrow zone in between continuous energy states which is called the band gap (E_g). The band gap ($E_{g,BULK}$), ranging from a fraction of an eV up to a few eV, lies between the valence band and the conduction band. When external energy in terms of heat, photon, voltage or etc. is provided to the valence band electrons, they jump to the conduction band leaving a positive *hole* behind. The valence band hole and the conduction band electron form an *exciton* pair and the distance between them is called *Exciton Bohr Radius* (EBR). When the size of the particle is comparable with EBR and the wavelength of the electron wave function, the energy levels are discrete rather than being continuous which is referred as quantum confinement where Heisenberg's uncertainty principle overrules the temperature and material specific properties.⁴⁹ This is explained by the restricted motion of the charge carriers (electron and hole) and the resultant solution of the Schrödinger equation. In a bulk semiconductor, the motion of the charge carriers is unrestricted along all 3 directions. However, when one or more of the dimensions of the particle is reduced to nanometer scale quantization of the carrier energy is observed.

When the electrons are confined in a plane where they have no freedom of motion in the third dimension, *quantum wells* are formed. When electrons are free only in one dimension but constrained in the other two dimensions, the structure formed are *quantum wires*. *Quantum dot (QD)* is formed when electrons have no freedom in any of the three dimensions (Figure 1.5). Hence, quantum dots are considered as zero-

dimensional molecules. For QDs, with the infinite-depth well approximation the energy of the carriers in a cuboid-shaped dot of dimensions L_z , L_y and L_x is given by the following relation which implies fully quantized and discrete energy levels;¹

$$E_{n,m,l} = \frac{\hbar^2 n^2}{8m \cdot L_z^2} + \frac{\hbar^2 m^2}{8m \cdot L_x^2} + \frac{\hbar^2 l^2}{8m \cdot L_y^2}$$

where $n, m, l = 1, 2, 3, \dots$ principal, magnetic and azimuthal quantum numbers, respectively. (Eqn. 1.4)

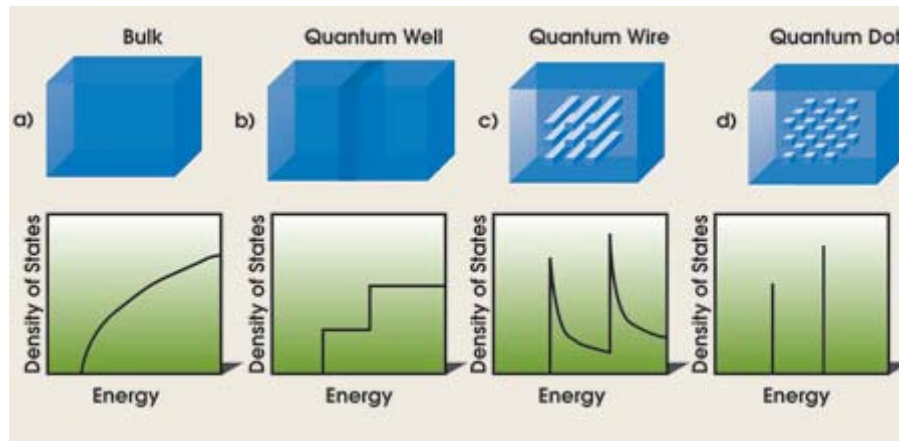


Figure 1.5 Quantum confinement effect and the corresponding density of states⁵⁰

The electrons in the valence band are excited to higher energy conduction band upon external stimuli like photon, heat or voltage which is called absorption. As the electron falls back to the valence band to recombine with the hole, some of the electromagnetic radiation corresponding to the energy it loses during the fall is emitted

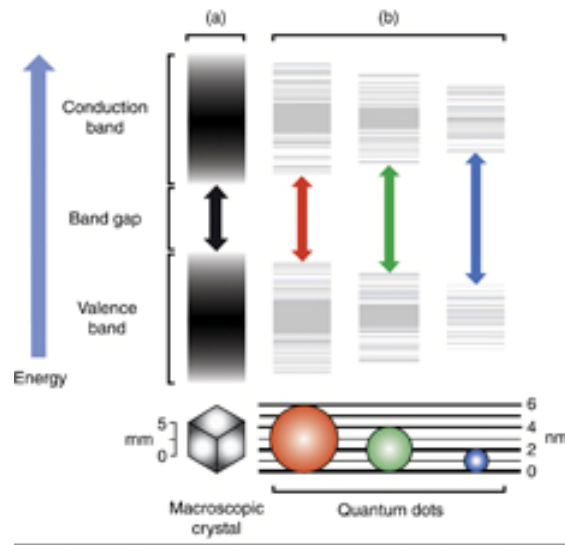


Figure 1.6 Difference of the energy levels of bulk material and QDs and size dependence⁵¹

in the form of photons. This is called the *radiative recombination* and results in the fluorescence of the particles. The non-radiative decay occurs when the electrons combine with the traps/ defects in the structure result in phonons in the form of lattice vibrational wave. However, this non-radiative energy loss is very small in quantum dots due to the fact that phonon scattering rates significantly decrease with increasing energy-level separation as proposed by Bawendi *et al.*⁵² For bulk semiconductors, both the energy absorbed and emitted is fixed since they both depend on the band gap energy. However, the energy of emission is lower than the energy of absorption since some of the energy absorbed is lost through the non-radiative path. Hence, the lowest peak in the absorbance spectrum is blue shifted according to the corresponding emission peak which is called the ‘*Stokes shift*’.

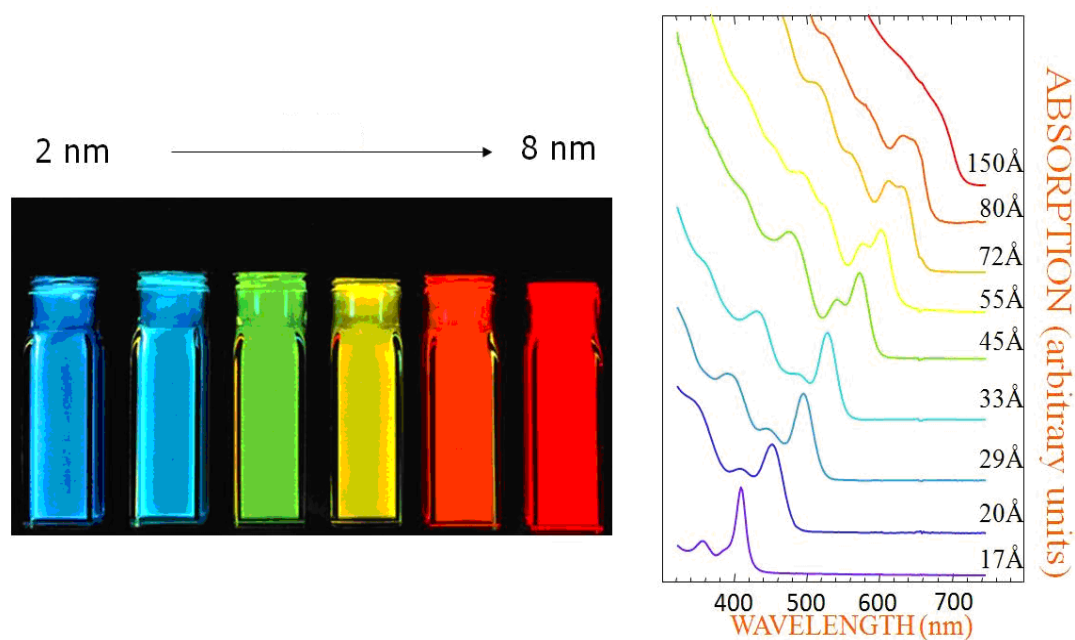


Figure 1.7 Tunable optical properties of QDs. (nanocluster.mit.edu/research.php)

The strength of the QDs in optics results from the fact that their band gap is not fixed as the bulk counterparts but depend on the dimensions of the molecules. Hence, both absorption and fluorescence spectra as well as the luminescence color can be tuned by adjusting the size of the QDs. As the size of the quantum dot decreases, and the electrons in the quantum dot are confined in even smaller regions, the energy difference of valence band and the conduction band increase. The absorption and fluorescence spectra are blue shifted with the increasing energy difference as the crystal size decreases (Figure 1.7).

1.2.2 Synthesis and Basic Characterization of Colloidal QDs

Colloidal QDs of the interest in this study are CdS, CdTe and CdTe/CdS which are mostly synthesized by wet chemistry where the growing nanocrystals are stabilized by a suitable capping agent (or ligand) in solution. Choice of the capping agent is an important step since it both determines the solubility of the QD in the synthesis environment and adheres on the surface of the growing crystals providing a shell that stabilizes the QD. Hence, the growth kinetics, size and composition of the QDs can be controlled by ligands. During the crystal growth, crystals smaller than a critical size dissolve while the larger crystals grow. Then the size distribution depends more on the larger particles than the critical size and smaller particles are growing faster than the larger ones. Close to the end of the reaction, when the ligand concentration is significantly reduced; the situation changes and the smaller crystals start to disappear while the larger ones continue to grow. This kinetics is proposed by Alivisatos, known as Ostwald ripening.⁵³ Ligands also cover the surface defects and trap sites hence decrease the extent of the non-radiative transitions which render the QD emit fluorescence in higher yields (quantum yield, QY).

There are two main routes in the wet synthesis; organic and aqueous. Most popular method is the organic TOPO synthesis developed by Bawendi and Alivisatos.⁵⁴ In this method organic solvents such as trioctylphosphine (TOP) or trioctylphosphineoxide (TOPO) or a mixture of TOP and TOPO are used as ligands at high temperatures to yield hydrophobic, monodisperse QDs with high emission yields. However, these nanoparticles suffer from decrease in the QY, low stability and size increase when they are extracted into aqueous solutions which is necessary for many biological applications.⁵⁵ The direct aqueous preparation technique was developed to overcome these drawbacks mostly using hydrophilic thiols to passivate the surface. In this system, bifunctional ligands are preferred such as thioacetamide⁵⁶, cysteine⁵⁷, mercaptoethanol⁵⁸, mercaptoacetic acid⁵⁹, mercaptopropionic acid⁶⁰ since –SH end group adhere on the surface while the other functional group is responsible for the

solubility/stability in the solution. In an effort to improve optical and oxidative properties, core/shell structures are being developed such as CdSe/CdS, CdTe/CdS.. In these synthesis CdS shell is formed around the core by addition of a sulfur source such as Na₂S or decomposition of thioacetamide, thiourea or dimercaptosuccinic acid (DMSA) which yields a slow release of sulfur.⁶¹

The most important and simplest characterization technique of synthesized QDs are to obtain absorbance and fluorescence spectra of the particles. Absorption spectra of QDs consist of overlapping peaks that corresponds to transitions between different exciton energy levels. The wavelength of the first excitonic transition of QD is the *absorption onset* which depends on the particle size as stated in the previous section. This size dependence of absorption was first studied by L.Brus and he proposed a relation which is used for the size calculation of the particles today.⁶² The details of the calculation is given in the Appendix. Fluorescence spectra display the position and the intensity of the emission. The spectrum is a Gaussian shaped curve and the bandwidth of this curve, *Full width at Half Maximum (FWHM)*, is used to comment on the particle size distribution. Smaller FWHM implies a narrower size distribution for QDs. From the area under this curve the efficiency of the fluorescence is calculated. The efficiency of the fluorescence-the quantum yield (QY)- of the quantum dots is defined as the percentage of the absorbed photons that resulted in an emitted photon. It is estimated in comparison with a reference fluorophore with known quantum yield according to the following equation⁶³;

$$QY = QY_R \frac{F A_R n^2}{F_R A n_R^2}$$

where F is the area under the fluorescence curves, A is the optical density at the excitation wavelength, n is the refractive index of the solvent and subscript R refers to the reference material. Rhodamine 6G (for CdTe) and Rhodamine B (for CdS) were used as references.⁶⁰

(Eqn 1.5)

1.2.3 Bio-Applications of QDs

Controllable emission band together with the high quantum yields increase the interest in quantum dots to be used instead of conventional organic fluorophores in bio-applications.⁶⁴ In addition, QDs find place in biological applications where especially long-term tracking is needed because of their higher photostability towards photo bleaching than organic fluorophores (Figure 1.8).⁶⁵ One of the other most striking features of QDs is the wide absorbance band makes it possible to excite emitting QDs at different colors at a single wavelength and leads to developments of microchips, sensors/ biosensors and multiplexing assays. They are also used in fluorescence resonance energy transfer analysis, gene technology, fluorescent labeling of cellular proteins, pathogen and toxin detection, *in vivo* animal imaging and tumor biology investigation.^{66 67}

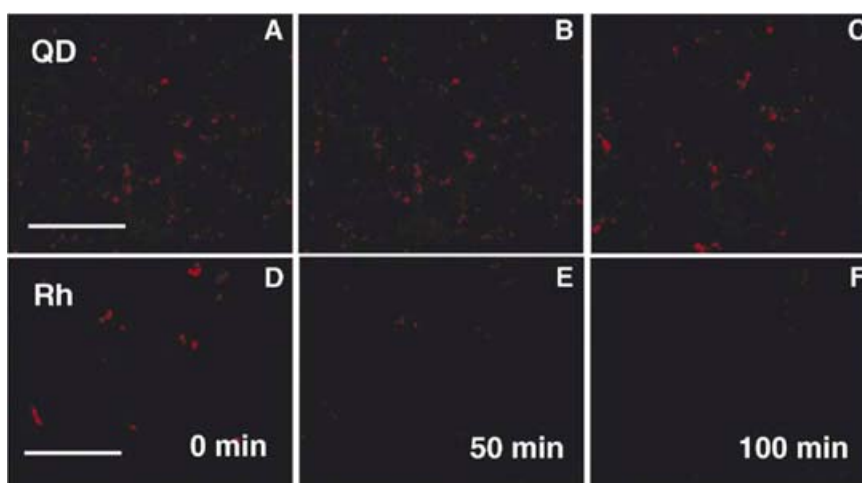


Figure 1.8 Comparison of QD and rhodamine long-term photostability. QD–DNA conjugates a) after 3 hour of transfection b) after 3 hour 50 min. of transfection c) after 4 hour 40 min transfection. Rhodamine complexes of DNA d) after 3 hour of transfection e) after 3 hour 50 min. of transfection f) after 4 hour 40 min transfection.⁶⁵

However, these bio-systems suffer from certain drawbacks such as immunogenicity, heavy metal release and toxic capping agents. It is suggested that the toxicity of the bare CdS stems from reactive oxygen species (ROS) production, GSH depletion, and Cd^{2+} release.⁶⁷ To reduce the cytotoxicity, mostly used method is to passivate the surface of the QDs with different ligands or shell such as CdS/ZnS core/shell QDs.⁶⁸

1.3 Purpose and Objectives

There is a great interest in obtaining advanced materials with altered morphologies, since often shape and size influences the properties of nanomaterials and applications.⁶⁹⁻⁷¹ Control and modification of these properties are of great interest. Recently, there is a growing interest in the template-assisted synthesis of the layered double hydroxides using various surfactants to alter material morphology which is usually determined during the growth. Besides, these surfactants are intercalated between the layers of LDH sheets. Although the literature contains significant amount of work with Mg-Al LDHs, examples are scarce for Zn-Al LDHs. In this study, we want to explore the influence of the surfactant type and concentration as well as the reaction time on the Zn-Al LDH morphology synthesized via urea hydrolysis method by using sodium dodecyl sulfate and sodium laurate as a guest anion.

In addition, we want to improve the features of LDHs that will be used in bio-applications by adding a tracking tool, namely QDs for optical tracking. Such character would allow tracing of the LDH nanohybrids to understand the fate of these clay nanohybrids inside the cells. Hybrids are constructed in the form of QD intercalated LDHs. This LDH/QD promise high potential in pharmaceutical and biological applications. A major requirement of the procedures used to form the composites is that they do not render the particles unusable for applications. Hence, optimization of the surface characteristics of the particles is also of primary importance for the successful

application of these composite particles. The luminescence intensity of the ODs decreases with time although they are more stable than organic fluorphores.⁶⁴ It has been shown that the luminescence properties can be enhanced by surface passivization with organic molecules⁷², forming a lower band gap-energy semiconductor shell⁷³ or an inorganic Cd(OH)₂ shell⁷⁴ around the core QD. Hence, part of this thesis is devoted to compare QD properties prepared in solution versus within the interlayer galleries of LDHs. This includes the investigation of size, luminescence, stability and toxicity evaluations. It is within the goals of this thesis work to determine whether being inside the LDH galleries would enhance the optical properties of the QDs and their stability. Furthermore, being inside the LDH galleries may help to enhance the biocompatibility by preventing the cadmium release or production of the ROS. Thus, in the second part of this work the formation of LDH/QD hybrid systems and the properties of these hybrids were studied.

Chapter 2

MORPHOSYNTHESIS of Zn-Al LAYERED DOUBLE HYDROXIDES

There is a great interest in obtaining advanced materials with altered morphologies, since often shape and size dictates the properties and applications.⁶⁹⁻⁷¹ Layered double hydroxides have received considerable interest due to their wide range of application areas as described in chapter 1.

Conventional co-precipitation technique in the presence of NaOH⁷⁵ or even urea synthesis method³ gives rise to hexagonal platelet LDHs as shown in Figure 2.1. These hexagonal platelets tend to form ‘rosette’ aggregates, especially in relatively low urea or hexamethylenetetramine (HMT) concentrations.⁷⁶ (Figure 2.3) Self-assembled structures can be used as a template to manipulate the morphology of the materials. Recently, there is a growing interest in the template-assisted synthesis of the layered double hydroxides with surfactants.

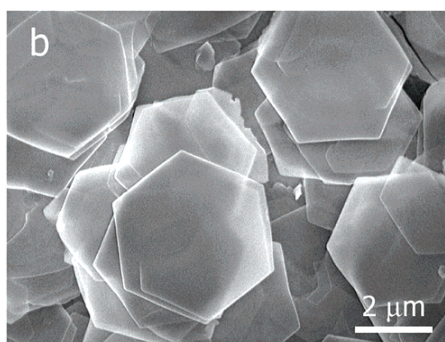


Figure 2.1 SEM images of the Co-Al-CO₃ LDH sample.³

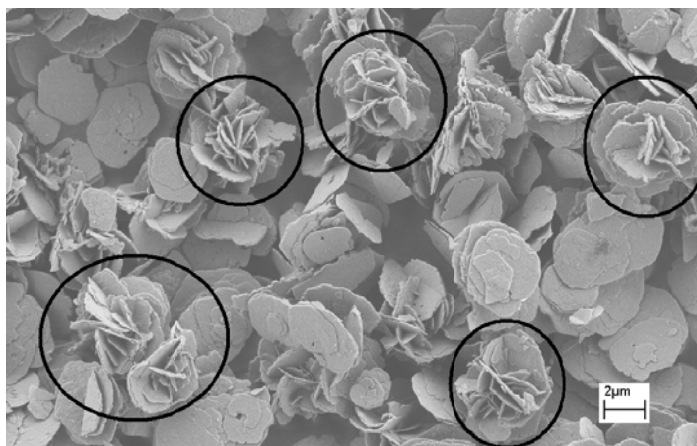


Figure 2.2 SEM micrograph of Zn-Al-CO₃ LDH synthesized by urea method in this study. 'Rosette' aggregates.

Surfactants are surface-active reagents that prefer to be at the air-water interface and result into a decrease in the surface tension with increasing concentration in the solution. They are composed of two well-defined, distinct regions: one oil soluble tail which usually consists of long hydrocarbon chains and one water soluble, polar head group. Surfactants usually have low solubility in water and they spontaneously form aggregates of well-defined structures such as spherical micelles, cylinders, bilayers, inverted micelles and even liquid crystal phases, etc. above certain concentrations called critical micelle concentration (CMC).^{77,78} Above CMC, the surface tension remains nearly constant and the micelles are spherical in shape with hydrophilic region on the outside and the hydrophobic part in the interior. The shape of the micelles and the type of the aggregate structure formed depend on many factors such as surfactant structure, the solution concentration, adding of electrolytes or not and a factor called as critical packing constant as proposed by Israelachvili *et al.* given by the equation 2.1⁷⁹

$$P_c = V/a_0 l_c$$

V is the volume of the hydrophobic part of the surfactant,
 a_0 is the effective area per head group,
 l_c is the length of the hydrocarbon chain.

(Eqn. 2.1)

Spherical micelles are formed for $P_c \leq 1/3$ and cylindrical (rod-like) micelles are formed for $1/3 < P_c \leq 1/2$ and bilayers preferentially form for $1/2 < P_c \leq 1$. SDS with a single hydrocarbon chain and a sulfate head group has a P_c value of 0.37⁷⁷ which indicates a tendency to form spherical micelles in water at the critical micelle concentration. P_c of SL having a carboxyl head group is calculated to be 0.42⁸⁰ indicating aggregate formation in the form of cylindrical micelles. However, the effective head group area, a_0 varies depending on the repulsion interactions between the head groups and hydrophobic attraction. P_c increases with increasing surfactant concentration due to the decrease of bound water.⁷⁸ Hence at high concentrations, the micelles might combine into cylindrical forms, elongated ‘worm-like’ structures and convert into lamellar sheets which might be of various lengths.⁸¹ Cylindrical micelles at high concentrations also tend to form into hexagonal packing.⁷⁷ Furthermore, addition of the electrolytes into surfactant solutions increases the screening of the electrostatic repulsion of the head groups giving rise to an increase in P_c but a decrease in CMC. The structure of the aggregates hence changes also upon addition of electrolytes. It is reported that SDS forms ‘prolate spherocylindrical’ micelles far from CMC, at high [SDS], high [salt], and low temperature by characterizing the scattered light intensity with cumulants analysis (Figure 2.2).⁸² It was deduced from the fact that the mean hydrodynamic radius (R_h) of the SDS micelles increases from 50 Å to 200 Å when SDS amount is increased from 3CMC to 185CMC at 0.8M NaCl, at 20°C. R_h increases from 23 Å to 100 Å when temperature is decreased from 70°C to 18°C at an SDS concentration of 150CMC in the presence of 0.6M NaCl.

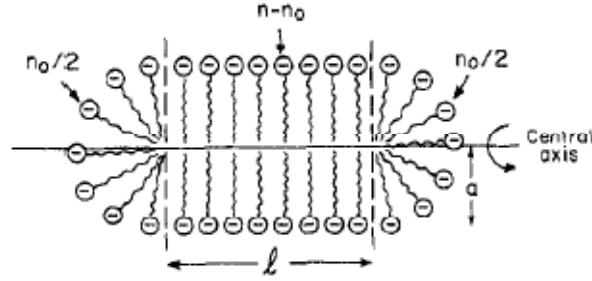


Figure 2.3 ‘Prolate spherocylindrical’ micelle with hemispherical handcaps proposed by Missel *et al.*⁸²

It has been also shown that the at 0.3 M NaCl, Gibbs energy of micellization for SDS goes from $\Delta G_m^{mic} / k_B T = -13.0$ without salt to $\Delta G_m^{mic} / k_B T = -14.2$ per mol surfactant accounting for the decrease in CMC according to the relation shown in Equation 2.2.^{77, 83}

$$\Delta G_m^{mic} = RT \ln CMC \quad (\text{Eqn. 2.2})$$

The CMC of pure SDS in water at 25°C is 8.3 mM⁸⁴ and that of SL is 25mM⁸⁵. In addition to this first critical micelle concentration (1st CMC), a second concentration point is defined where again a change in the physical properties of surfactant solutions occur (2nd CMC). The 2nd CMC is reported as 65mM for pure SDS at 25°C determined by conductivity measurements⁸⁶. Kodama and Miura also found evidence that supports the view which suggests spherical SDS micelle with nearly constant molar volume at concentrations between 1st CMC and 2nd CMC and shape transformation into an asymmetrical sphere at 2nd CMC accompanied by a decrease in the molar volume. In addition they observed lowered 2nd CMC with addition of NaCl.

In the view of the aforementioned literature surfactant intercalation might be regarded as a transition from the micelle form into lamellar form creating⁸⁷ diverse structures in the intergallery of the LDHs through self-assembly into monolayers, tilted-monolayers, bilayers, tilted-bilayers, or interdigitated systems^{25, 88} and distinct morphology of the nanocomposites.⁸⁷ ‘Curved platy’ morphology was reported by Ogawa and Asai²⁵ for LDHs intercalated with deoxycholate and discussed that this interesting morphology stems from the cooperative organization of deoxycholate and cationic hydroxides. Band-like structures were observed for Mg-Al LDHs that were prepared in the presence of dodecyl sulfate by Valim and co-workers and they attributed this result to the aggregation of the LDH under surfactant influence.⁸⁹ Later, Braterman and Xu observed similar bar-like and curved sheets with dodecylbenzene sulfonate for Mg-Al LDH and suggested that hydrophobic interactions favoring the growth in the *c* direction are responsible for these observations.⁹⁰ Leroux *et al.* synthesized alginate intercalated Zn-Al LDH with stacked layers of ‘tubular’ shape.²⁰ Duan and co-workers showed that curved ‘fibre-like’ morphology can be obtained via precipitation with chitosan for Ni-Al LDH.¹⁷ Recently, synthesis of ‘pompon-like’ spherical morphology of curved Ni-Al-alginate sheets by the urea method was reported.⁹¹ The curved sheets with a thickness of about 5-10 nm were intercrossed and the structure resembles to that of corals. Increasing the reaction time did not show significant change in the thickness but increase in the lateral dimension. Hence, preferential crystal growth along *a* dimension was proposed in the presence of the alginate with the urea method. Xu and Gunawan prepared also coral-like microspheres of Mg-Al LDH by solvothermal method in a nonaqueous polar solvent-surfactant system of ethylene glycol-methanol-dodecyl sulfate.⁹² They argue that the presence of dodecyl sulfate is also crucial for inhibiting the crystal growth by modifying the surface of the particles. Hu and O’Hare showed that the aspect ratio of the LDHs can be adjusted.⁹³ By using reverse microemulsion method, they obtained belt-like and rod-like Mg-Al LDH upon addition of

the dodecyl sulfate solution at different stages of the synthesis. Mg-Al LDH with deviations from the hexagonal platelet structure by surface irregularities and different surface textures were obtained by F.R. Costa *et al.*⁹⁴ via intercalation of laurate, dodecyl sulfate, dodecylbenzene sulfonate and bis(2-ethylhexyl)phosphate.

Besides determining morphology, surfactants are also important for various applications since most of them require organic-inorganic composites. To prepare organic-inorganic composites or polymer blends efficiently, LDH should be compatible with the organic molecules which can be achieved by introducing some hydrophobicity to the hydrophilic nature of the LDH. Thus, surfactants having both hydrophilic and hydrophobic groups play an important role in the preparation of the hybrid LDHs.

Although the literature contains significant amount of work with Mg-Al LDHs, examples are scarce for Zn-Al LDHs and usually method is not the urea hydrolysis. For example, Ogawa *et al.* uses hydrothermal method with gibbsite and zinc oxide as starting materials to construct Zn-Al LDH intercalated with SDS.²⁵ A significantly different morphology other than the irregularities hasn't been reported. In this study, the influence of the surfactant type and concentration as well as the reaction time on the Zn-Al LDH morphology was investigated. Zn-Al LDHs were synthesized via urea hydrolysis method in the presence of sodium dodecyl sulfate or sodium laurate at concentrations which are below and above the critical micelle concentration of the surfactants.

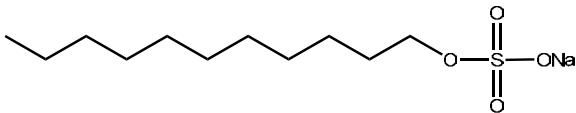
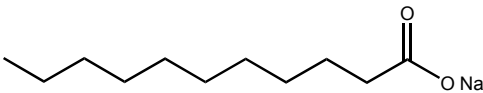
2.1 Experimental

2.1.1 Materials

All the chemicals used were of analytical grade or of the highest purity commercially available. Aluminium nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), urea ($\text{CH}_4\text{N}_2\text{O}$), dodecyl sulfate sodium salt (SDS) were purchased from Merck. Zinc nitrate hexahydrate

($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), and lauric acid were purchased from LaCheMa and Fluka, respectively. Sodium salt of the lauric acid (SL) was obtained through heating the acid in 1:1 NaOH (Aldrich) solution. Double distilled, high purity water was used from Milli-Q water (Millipore) system. The chemical structures and formula of the surfactants used for the synthesis are provided in Table 2.1.

Table 2.1 Chemical structures of the surfactants used

Chemical Name	Structure	Functional Group
Sodium Dodecyl Sulfate		Sulfate
Sodium Laurate		Carboxylate

2.1.2 Synthesis of Zn-Al LDHs intercalated with Surfactants

Surfactant intercalated Zn-Al layered materials were synthesized by the urea hydrolysis method as reported earlier⁹⁵. In a typical synthesis, 10mM Zn^{2+} and 5 mM Al^{3+} salts with a mole fraction of $\text{Zn}^{2+}/\text{Al}^{3+}=2$ were dissolved in distilled water under Ar in a 4-necked round bottom flask fitted with a mechanical stirrer. An appropriate amount of either SDS or SL was added into the above solution. Finally, the ammonia releasing agent-urea was added with a mole fraction of $\text{urea}/\text{Zn}^{2+}=3.5$ and the mixture was heated at 90°C for 120hr. Samples from the mixture was taken in 24 hour intervals for analysis. A control sample without addition of any surfactant was prepared under identical conditions. LDH in the form of a white precipitate was removed from the white slurry formed in 3 hours,

through centrifugation at 3900rpm for 30 min. It was washed with decarbonated water four times and dried under vacuum before analysis.

The intercalation of SDS was performed at three different concentrations: 5, 15, 100 mM. The reaction with 15mM SDS was also repeated with a zinc plate in the reaction vessel. For SL intercalation, surfactant concentration was varied from 15 mM to 100 mM at $\text{Zn}^{2+}/\text{Al}^{3+}=2$. Reactions were also performed with $\text{Zn}^{2+}/\text{Al}^{3+}$ ratio of 1, 4 and ∞ at 100 mM SL concentration.

2.1.3 Instrument and Characterization

The crystal structure and crystallinity of the samples were analyzed by powder X-ray diffraction (XRD) with HUEBER G670 diffractometer with a germanium monochromator and Cu-K α radiation at 1.54056Å in 2θ range from 5° to 100° with 0.005° interval. Data were analyzed by using STOE WinXPOW software. A Bruker axs advance powder diffractometer fitted with a Siemens X-ray gun and equipped with Bruker axs Diffrac PLUS software using CuK α radiation was also used in Sabancı University. The sample was rotated (20 rpm) and swept from $2\theta = 5^\circ$ through to 80° using default parameters of the program. The X-ray generator was set to 40kV at 40 mA. a Rigaku D/MAX-Ultima+/PC X-ray diffraction equipment was used for the analysis of some powders in Boğaziçi University and Rigaku MiniFlexII was used at Koc University for some of the analysis. The FT-IR spectra were recorded on JASCO FT-IR-600 PLUS spectrometer using KBr pallets. Raman spectra were obtained from BRUKER FT-Raman RFS100 spectrometer with a Nd:YAG laser source and Ge diode detector up to 4000cm⁻¹. Metal amounts were determined by using Inductively Coupled Plasma analysis on a SPECTRO GENESIS EOP ICP. Solutions in triplicates were prepared by dissolving the samples in hot aqua regia. Thermogravimetric Analysis (Shimadzu TGA 50H) was

performed on dried powders to analyze the surfactant and water content. The morphology of the powders was examined with a Leo Supra 35VP Field emission scanning electron microscope, and Leo 32 electron dispersive spectrometer software was used for images and analysis. Imaging was generally done at 2-5 keV accelerating voltage, using the secondary electron imaging technique in Sabancı University. XL30 ESEM-FEG/EDAX system was also used in Boğaziçi University. Some of the samples were analyzed after coating with platinum by JEOL JSM 7000 in İstanbul Technical University.

2.2 Results and Discussion

2.2.1 Synthesis of SDS intercalated Zn-Al LDH by urea method

In this study, recently developed urea hydrolysis method was successfully applied to the synthesis of SDS intercalated Zn-Al LDHs with different morphologies.⁹⁵ The crystallinity of the Zn-Al-CO₃ and SDS (100mM) intercalated LDHs that were synthesized under the same conditions, was verified by the XRD analysis of the powders (Figure 2.4). The characteristic intense basal reflection peaks together with the appearance of higher order peaks indicate a high degree of crystallinity for both types of samples. The sharpness of the peaks suggests ordered and regular stacking of the sheets. XRD of the Zn-Al-CO₃ displays $d_{003}(11.51^\circ)$, $d_{006}(23.46^\circ)$, $d_{009}(37.40^\circ)$, $d_{012}(34.65^\circ)$, $d_{015}(39.30^\circ)$, $d_{018}(46.91^\circ)$, $d_{110}(60.43^\circ)$, $d_{113}(61.80^\circ)$ crystal planes with the basal spacing of 0.768nm. The very similar basal distances due to the attractive force between positively charged brucite-like sheets and the interlayer anions are observed in literature for similar LDHs. The appearance of the (012), (015) and (018) reflections indicate 3R₁ polytype with rhombohedral symmetry which is believed to be the structure of the most carbonated LDH. The hydroxyl groups of the upper and the lower layer can form hydrogen bonds with the carbonate

oxygens in the prismatic alignment of the hydroxyls.⁹⁶ Basal spacing c_0 is calculated from the Bragg's equation (Eqn. 2.3), accounts for the interlayer gallery distance since it is equal to the thickness of one brucite-like layer plus one interlayer.⁹⁷ Intercalation of the anionic surfactants depending on their size, functional group and alkyl chain length might result in a change in the interlayer gallery distance. If the interlayer distance increases the basal reflection peak is shifted towards lower angles. XRD of the SDS intercalated sample shows $d_{003}(4.21^\circ)$, $d_{006}(6.51^\circ)$, $d_{009}(9.98^\circ)$, $d_{110}(60.43^\circ)$ crystal planes with the basal spacing 2.097 nm as expected. This basal spacing of 2.097 nm is smaller than the reported values 2.69 nm for Cd-Cr and 2.74 nm for Zn-Cr LDH⁹⁸, 2.80-2.78 nm for Mg-Al LDH prepared by urea hydrolysis and 2.72⁹⁹, 2.68¹⁰⁰, 3.24-2.92 nm⁹² for the Mg-Al LDH prepared by co-precipitation, , 2.6 nm for the Mg-Al LDH prepared by reverse microemulsion⁹³ and 3.30 nm for the Mg-Al LDH prepared by anion exchange⁹⁴. However, it is very close to the basal spacing of 2.091 observed for the Mg-Al LDH prepared by anion exchange method.¹⁰¹ The disappearance of the peak at $2\theta = 11.51^\circ$ implies that no carbonate is intercalated as an impurity from the hydrolysis of urea which might not be the case if ion-exchange mechanism was used¹⁰¹. The saw-toothed peaks at around $2\theta = 34^\circ$ and $2\theta = 61^\circ$ of both samples stem from the turbostratic disorders which offers a relatively random packing of layers.⁹⁶ A broad peak centered at around $2\theta = 22^\circ$ appears for the SDS intercalated sample which was found in delaminated LDHs. The formation of this peak was attributed to the stacking of the alkyl chains in the interlayer gallery by Iyi *et al.*⁹⁷ B.Li *et al.* proposes that interlayer distance is so enlarged by the SDS intercalation that, the hybrid exhibits features of delaminated LDH.¹⁰⁰

$$d = \frac{\lambda}{2 \sin \theta} \text{ , where } d \text{ is the basal spacing, } \lambda \text{ is the wavelength and } \theta \text{ is the diffraction}$$

angle.

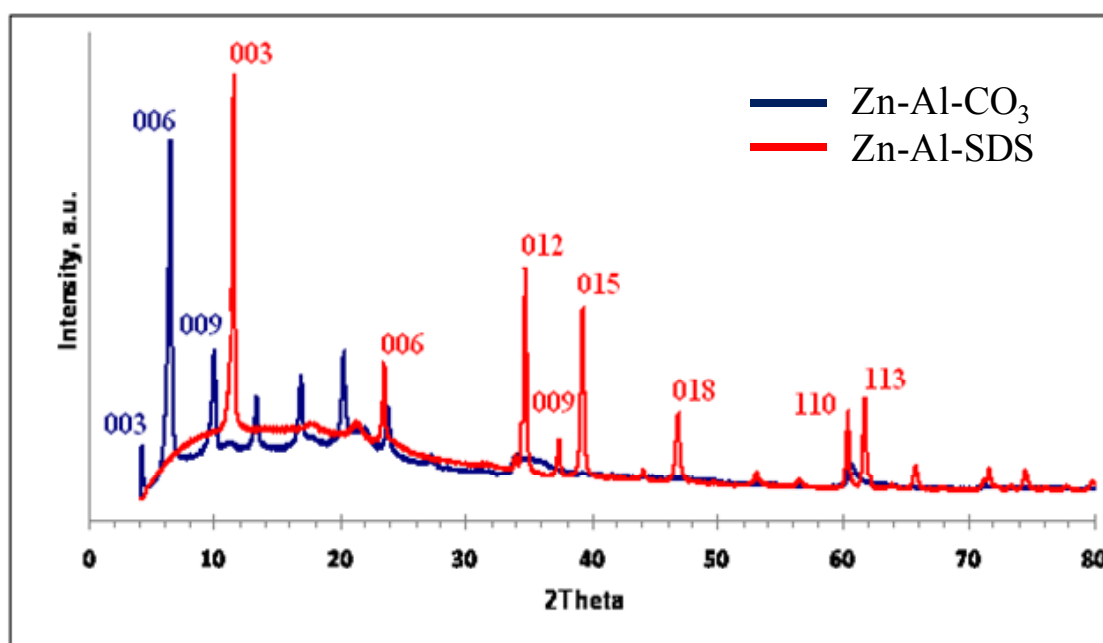
(Eqn. 2.3)

Table 2.2 Indexing the XRD parameters of CO₃ and SDS intercalated Zn-Al LDH

Sample	d_{003}	d_{006}	d_{009}	d_{110}	Gallery Height (nm)	Tilt Angle*	Cell parameters**	
	(nm)	(nm)	(nm)	(nm)			$a=b$ (nm)	c (nm)
Zn-Al-CO ₃	0.768	0.379	0.240	0.153	0.288	—	0.306	1.404
Zn-Al-SDS	2.107	1.356	0.888	0.152	1.627	49.8°	0.304	6.321

* Calculated from Eqn.2.4.

** Calculated for a rhombohedral unit cell by indexing $a=b=2d_{110}$ and $c=3 d_{003}$.⁹³

**Figure 2.2** XDR patterns of Zn-Al LDH synthesized with/without SDS.

The presence of the surfactant in the LDH structure was further verified by FT-IR spectroscopy (Figure 2.5). Free CO₃²⁻ anions in solution was reported to display three

different IR vibrations; out of plane bending mode (ν_2) at 880 cm^{-1} , asymmetric stretching mode (ν_3) at 1415 cm^{-1} and the in plane bending mode at 680 cm^{-1} ⁹⁶. The FT-IR peaks of the carbonate anion intercalated within the LDH sheets are shifted to lower wavenumbers and splitting of the bands due to the decrease in the symmetry are observed. In most cases the asymmetric stretching mode is observed around $1350\text{--}1390\text{ cm}^{-1}$ in CO_3^{2-} /LDHs. The

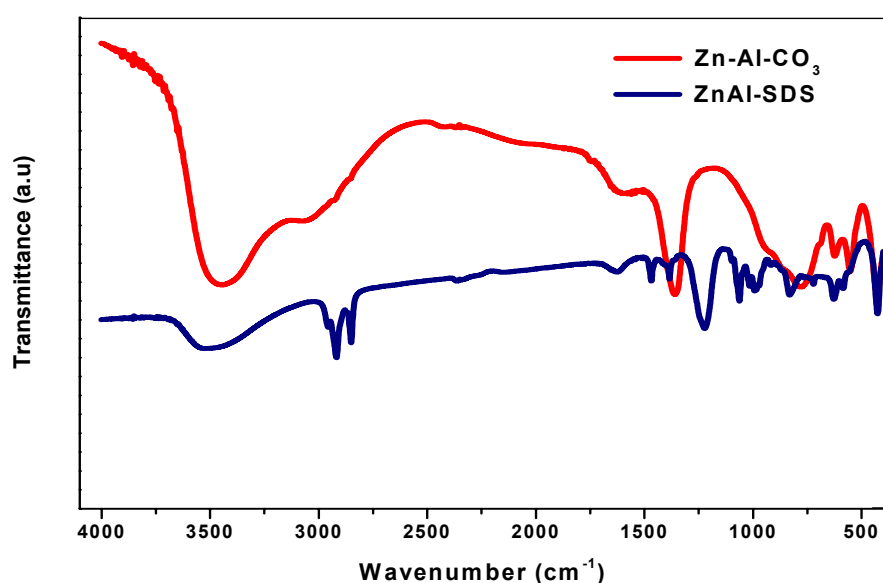


Figure 2.3 FT-IR spectra of Zn-Al LDH synthesized with/without SDS.

out of plane and in plane bending modes are reported to be observed around $850\text{--}880\text{ cm}^{-1}$ and $670\text{--}690$. FT-IR Spectra of Zn-Al- CO_3 and SDS intercalated sample respectively.⁹⁴ Hence, the observation of the very sharp peak at 1360 cm^{-1} without any apparent shoulder indicates the absence of the splitting of the ν_3 band suggesting a symmetric environment between the metal hydroxide layers.⁹⁶ The small shoulders around 688 cm^{-1} and 878 cm^{-1} correspond to the other vibration bands of the intercalated carbonate (ν_4 and ν_2

respectively). The broad band around $3200\text{--}3500\text{ cm}^{-1}$ is the characteristic O-H stretching band and the small shoulder around 3054 cm^{-1} is attributed to the H-bonded O-H stretching vibration (with the carbonates).⁹⁰ The weak band at 1616 cm^{-1} is due to the bending mode of the H_2O . The bands appearing at 781 , 628 , 554 and 428 cm^{-1} are caused by M-O stretching and the lattice vibrations of the metal hydroxide sheets. The FT-IR spectrum of the SDS intercalated LDH shows bands that belong to both surfactant and the metal hydroxide sheets. For the SDS, characteristic $-\text{CH}_2$ stretching bands were observed at 2958 , 2918 and 2985 cm^{-1} and the $-\text{CH}_2$ bending peak was at 1466 cm^{-1} . The symmetric vibration of the S=O was shifted from 1084 to 1064 cm^{-1} but the antisymmetric vibration of the S=O was at 1223 cm^{-1} similar to the free SDS.¹⁰⁰ The peak at 631 cm^{-1} is due to the C-S stretching. The band around 426 cm^{-1} results from the lattice vibrations of the metal hydroxide sheets and the broad band in the range $3200\text{--}3500\text{ cm}^{-1}$ originates from the O-H stretching vibrations mainly from the hydroxide layers. The characteristic carbonate vibrations are also observed at small intensities at 834 and 1385 cm^{-1} . The disappearance of the peak at $2\theta = 11.51^\circ$ in the XRD profile suggest carbonate might be absorbed during sample preparation. The appearance of a broad shoulder at 1622 (bending mode of H_2O) but the absence of the shoulder around $3000\text{--}3100\text{ cm}^{-1}$ suggests there is an interlayer water filling the voids rather than interacting with the carbonates⁹⁴ which further supports carbonate absorption after the reaction.

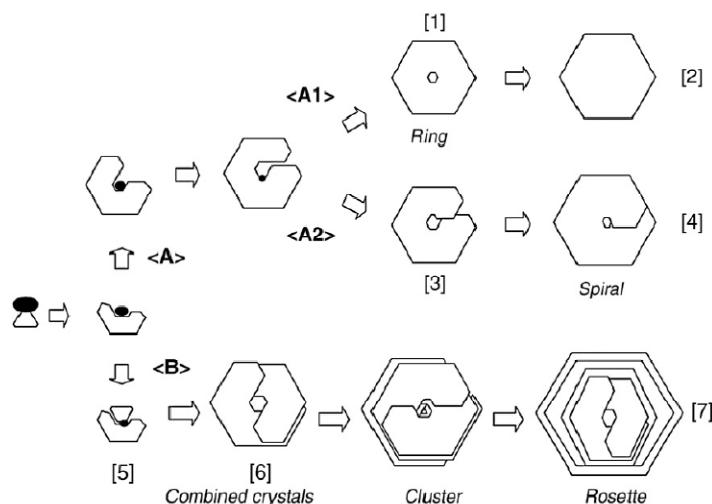


Figure 2.4 Proposed crystal growth mechanisms by Okamoto *et al.*²³

When SEM micrographs of the Zn-Al-CO₃ were analyzed, the crystal growth mechanism proposed by Okamoto *et al.* was observed.⁷⁶ It was reported during the synthesis of LDHs with the urea method; Al hydroxide would form during the initial stages of the reaction since Al hydroxide precipitates at lower pH values and act as seeds that would be converted into the LDH crystals. Okamoto *et al.* proposes that reacting with M²⁺, these seeds are depleted and converted into LDH (Figure 2.6): If the ends of the circle growing from the seeds meet at the same level during the circular crystal growth, the circle converts into a complete hexagonal plate and the mechanism is named as route<A1>. If the hole at the center due to the Al hydroxide seed depletion is preserved, a ring-like crystal forms. During the crystal growth, sometimes the ends of the circle does not meet at the same level and a spiral-like crystal is formed (route <A2>). It is argued that, at the low ammonia releasing agent concentrations, lesser Al hydroxide seeds are formed. This concentration effect might result in formation of two or more LDH crystals on the same Al hydroxide seed causing rosette structures (route).

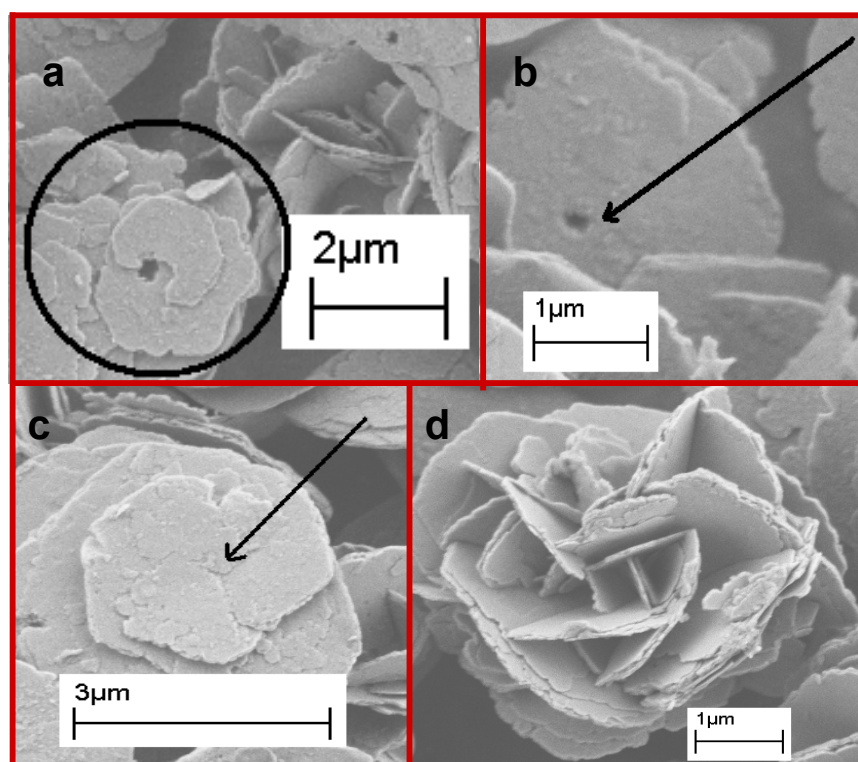


Figure 2.5 SEM images of Zn-Al-CO₃ synthesized in this thesis work showing intermediate growth stages proposed by Okamoto *et al.* a) ‘Spiral crystal’, LDH crystal growing around Al hydroxide seed. b) ‘Ring’ structure, the arrow indicates the center of LDH crystal where an Al hydroxide seed would have occupied. Growth route <A>/<A1>. C) ‘Spiral’ structure, combines spiral crystals. Growth route <A>/<A2>. d) ‘Rosette’ structure. Growth route .

All three kinds of imperfect crystals; ring-like, spiral-like and rosette aggregates besides perfect hexagonal platelets that were reported by Okamoto *et al.* are displayed in the SEM images of the Zn-Al-CO₃ LDH was produced in this thesis work (Figure 2.7). Furthermore, the incomplete crystal (Figure 2.7(a)), which corresponds to the intermediate structure <A> (Figure 2.6) in the <A>/<A1> route, supports the growth mechanism proposed. Sizes of the

Zn-Al-CO₃ crystals are around 2-3 μm similar to what was reported for the 24h to 80h reaction time with the urea method. The thickness of the CO₃-LDH slab was measured to be 125 nm, thicker than the observed values of 80-40 nm³ or 5-10 nm⁹¹ by Leo 32 electron dispersive spectrometer software (Figure 2.8).

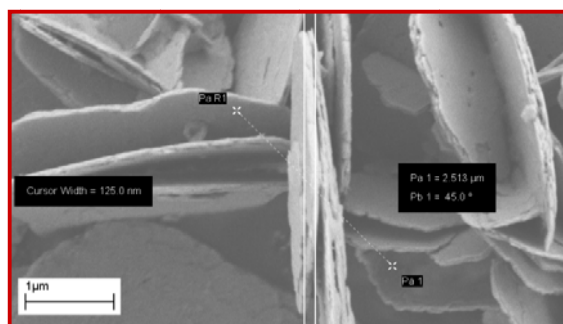


Figure 2.6 Thickness of the CO₃-LDH slabs.

Addition of 100mM SDS to the synthesis mixture produces a very different morphology that was not observed before to the best of our knowledge. Hollow rings resembling to the cereal ‘cheerios’ with much more smaller lateral size of about 35-50 nm were observed for the 24h reaction (Figure 2.9). Almost entire material is composed of stacked rings with only a few rounded platelets that are shown in the inset of the figure 2.9.(b). These ‘cheerios’ rings being spherical are different from the ‘ring-like’ intermediate structures-that are hexagonal in shape- formed during the crystal growth and filled completely later in the process that Okamoto *et al* proposed for LDH-CO₃. B.Li *et al.* observed curved or bent SDS intercalated LDH sheets which completely excluded the surfactant at prolonged reaction times upon intercalation with CO₃ in the solution from the urea hydrolysis, even though the bent morphology does not change.¹⁰⁰ Hence, to eliminate the fact that SDS is retarding the growth of the crystals so that the ring is an only

intermediate structure that would be converted into a platelet, effect of prolonged reaction time was analyzed. In addition, to be able to explain this interesting, unusual morphology concentration of surfactant was varied.

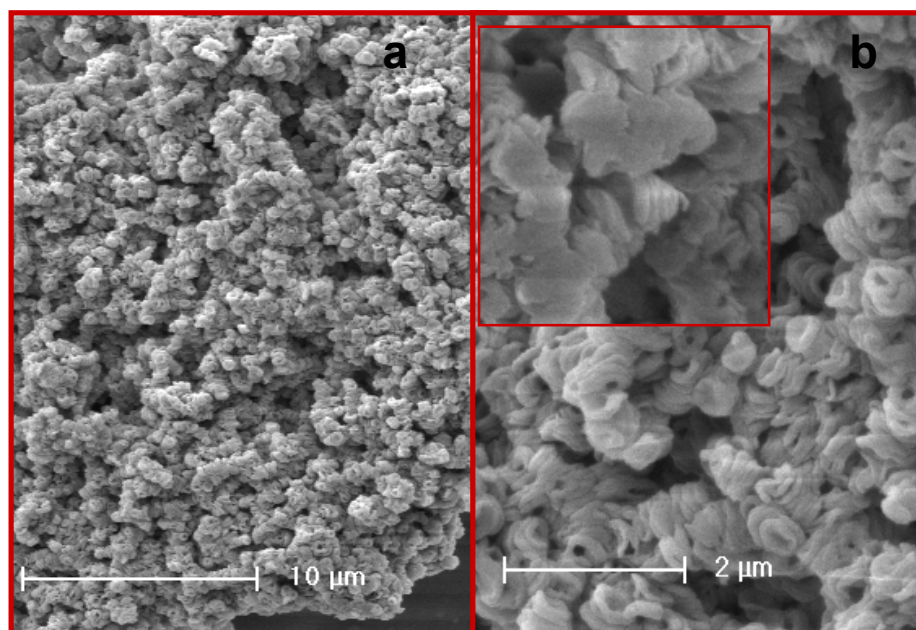


Figure 2.7 SEM images of the SDS(100mM) intercalated Zn-Al LDH(24h reaction) at different magnifications a) 5000X. b) 20000X.

2.2.2 Effect of SDS Concentration and Time on the Morphology of the Zn-Al LDH

The Zn-Al LDHs were synthesized in the presence of varying SDS concentrations. XRD profiles of the resulting solids are shown in Figure 2.10. The d_{003} , d_{006} , d_{009} , d_{110} reflections observed are at the characteristic 2θ values of SDS intercalated LDH as discussed in section 2.2.1. All samples exhibit turbostratic disorders with the saw-toothed peaks at around $2\theta = 34^\circ$ and $2\theta = 61^\circ$ and the broad peak centered at around $2\theta = 22^\circ$

appears in all of the XRD spectra. The indexing parameters and calculated gallery heights are displayed in Table 2.3.

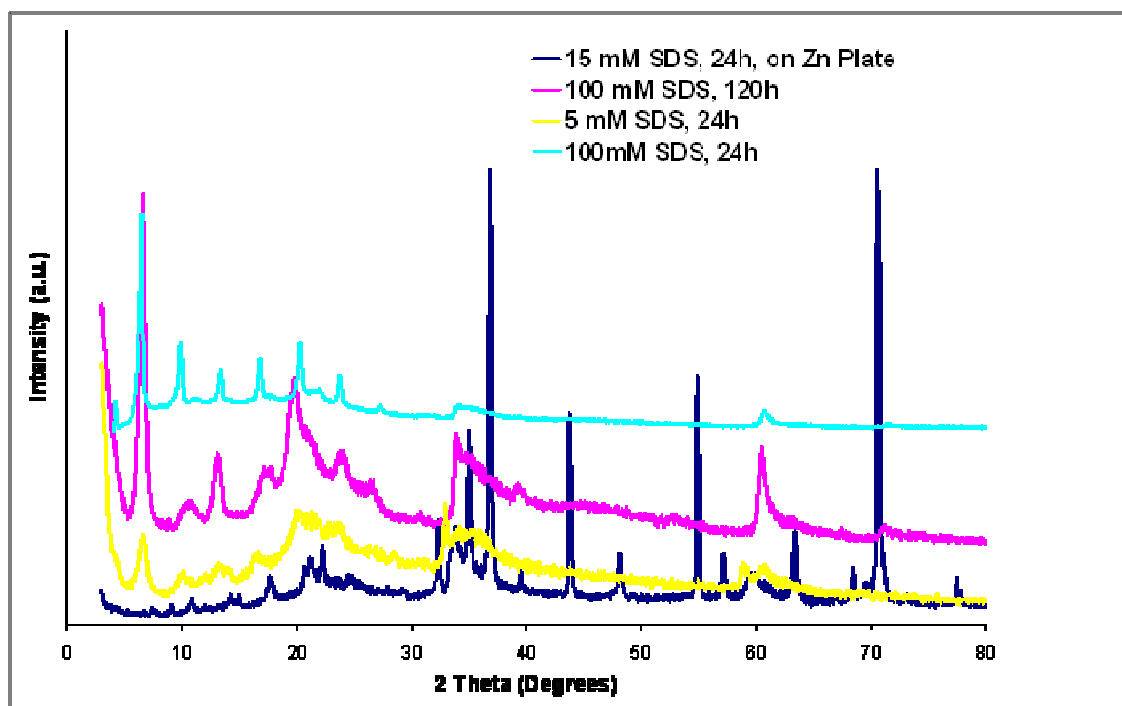


Figure 2.8 XRD Profiles of the SDS-intercalated Zn-Al LDH Samples.

Table 2.3 Indexing of XRD patterns of Zn-Al LDH synthesized in the presence of varying SDS concentrations

[SDS] (mM)	Time (h)	d_{003} (nm)	d_{006} (nm)	d_{009} (nm)	d_{110} (nm)	Gallery Height (nm)	Cell parameters [*] $a=b$ (nm) c (nm)	
0	24	0.768	0.379	0.240	0.153	0.288	0.306	1.404
5	24	2.852	1.334	0.864	0.152	2.372	0.304	8.556
15	24	2.850	1.358	0.880	0.152	2.370	0.304	8.550
100	24	2.107	1.356	0.888	0.152	1.627	0.304	6.321
100	120	2.903	1.356	0.815	0.152	2.423	0.304	8.709

^{*} Calculated for a rhombohedral unit cell by indexing $a=b=2d_{110}$ and $c=3 d_{003}$ ⁹³.

The difference in the basal spacing (d) is almost negligible with SDS concentration except for the 100mM sample but it also reaches similar values after prolonged time. Nevertheless, the reported basal spacing values for SDS intercalated LDHs vary in a considerable range and influences the arrangement of the surfactant inside the layers. These differences are attributed to the presence of adsorbed water⁸⁸, identity of the metals¹⁰² Mg /Al ratio¹⁰³, intercalation pH and the method of synthesis⁸⁷ in the literature. It can be seen from Table 2.4 that Zn / Al ratio decreases with SDS concentration in the synthesis mixture. The decrease in Zn / Al ratio corresponds to an increase in the layer charge density together with the intercalated SDS amount. The more surfactant in a restricted area causes a denser packing of the hydrocarbon chains inside the layers and hence a more tilted geometry resulting in lower d values as will be explained in the following discussion.¹⁰³

Table 2.4 Change in the Morphology of Zn-Al LDH with increasing [SDS]

[SDS] (mM)	[Zn ²⁺] (mM)	[Al ³⁺] (mM)	Zn ²⁺ /Al ³⁺ Mole Ratio ^a	Composition ^a	Basal Spacing ^b (nm)	Morphology
100	20	10	1.11	Zn _{0.53} Al _{0.47} (OH) ₂ (SDS) _{0.47} ·1.2H ₂ O	2.107	Stacked Rings
15	20	10	0.96	Zn _{0.49} Al _{0.51} (OH) ₂ (SDS) _{0.51} ·1.2H ₂ O	2.850	Coral-Like
5	20	10	0.89	Zn _{0.47} Al _{0.53} (OH) ₂ (SDS) _{0.53} ·1.1H ₂ O	2.852	Coral-Like
0	20	10	0.87	Zn _{0.47} Al _{0.53} (OH) ₂ (SDS) _{0.53} ·0.6H ₂ O	0.768	Platelets

^aMetal content was determined by ICP-OES. Content water was determined by TGA. SDS amount calculated according to the formula.

^bCalculated from Bragg's equation.

$\sin \phi = \frac{d - T}{l}$, where d is the basal spacing, T is the thickness of one layer, l is the length of the organic anionic surfactant and ϕ is the tilt angle. (Eqn. 2.4)

$d(\text{nm}) = 0.96 + 0.127 \cdot n \cdot \sin \phi$, where d is the basal spacing, n is the number of the carbon atom in the alkyl chain of the surfactant and ϕ is the tilt angle (Eqn. 2.5)

From the d values, the molecular arrangement of the surfactants inside the galleries are predicted which is generally determined by their chain length. The tilt angle of the alkyl chains from the normal of the metal sheets can be calculated by the Eqn. 2.4.^{97, 101} Assuming full length of dodecyl sulfate as 2.13 nm⁹⁸ and the layer thickness of the LDH as 0.48 nm, the tilt angle ϕ is calculated to be 49.8° (100 mM SDS, 24h) for perpendicular monolayer arrangement which is lower than the value found for monolayer arrangement of

surfactants in the interlayer by Meyn et al (56°).¹⁰⁴ They also propose a relation to predict the interlayer distance of the alkyl carboxylate and alkyl sulfonate LDHs represented by Eqn.2.5. The basal spacing d , calculated by using this equation with $\phi = 56^\circ$ is 2.22 nm is slightly higher than the observed value 2.10 nm. The difference of 0.12 nm with 2.10 nm might be attributed to a water molecule or and/or a sliding of the molecules as stated before by Iyi *et al*⁹⁷. However, the arrangement of the SDS in the intergallery cannot be explained by monolayer distribution for 5 mM, 15 mM and 100mM, 120 h samples. In fact, the packing of the hydrocarbon chains in between the LDH layers has been of considerable controversy. Y.Guo *et al.* envisions ‘a monolayer of SDS chains oriented perpendicularly

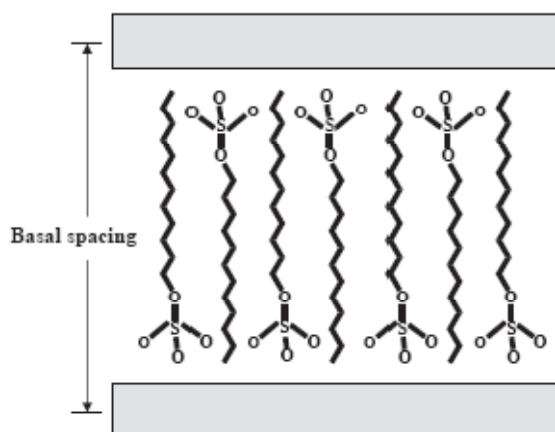


Figure 2.9 Monolayer arrangements of interdigitated surfactants.⁹⁸

and interdigitated in between the inorganic brucite-like layers’ for basal spacings of 2.69 and 2.71 nm (Figure 2.11).⁹⁸ Perpendicular monolayer arrangement is also proposed for SDS sodium 4-octylbenzenesulfonate, and sodium dodecylbenzenesulfonate .¹⁰⁵Li *et al.* argues basal spacings smaller than the sum of size of the surfactant and the thickness of the one of the layer are indicative of tilted monolayer arrangement where as the higher values

point out bilayer arrangement of the surfactant with interdigitated hydrocarbon chains.^{92, 100, 103} Several authors explain the packing with the same arguments.^{92, 97, 101} Itoh *et al.* also suggests a tilted bilayer packing mode for C18-carboxylate deduced from the 2-dimensional XRD analysis.¹⁰⁶ Meyn *et al.* calculates the basal spacings of the alkyl sulfate intercalated LDHs with the equations given in Equation 2.6 and Equation 2.7.⁸⁸ They suggest monolayer arrangement for surfactants with carbon atom number in the alkyl chain (n) = 14, 16, 18 and bilayers with $\phi = 22^\circ$ for n smaller than 14. Hence, a bilayer arrangement of SDS with interdigitated hydrocarbon chains where sulfate groups of the neighboring surfactant are attached to the upper and lower metal layer with angles $\phi = 28^\circ, 29^\circ$ is proposed for the 5 mM, 15 mM and 100mM-120 h samples, respectively.

$$\text{Monolayers: } d(\text{nm}) = 0.96 + 0.127 \cdot n \cdot \sin \phi, \quad (\text{Eqn. 2.6})$$

$$\text{Bilayers: } d(\text{nm}) = 1.42 + 0.254 \cdot n \cdot \sin \phi, \text{ where } d \text{ is the basal spacing, } n \text{ is the number of the carbon atom in the alkyl chain of the surfactant and } \phi \text{ is the tilt angle.} \quad (\text{Eqn. 2.7})$$

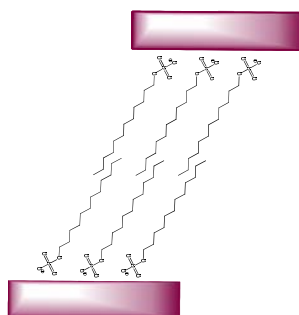


Figure 2.10 Probable arrangement of the SDS in the interlayer gallery.

In addition to differences in basal spacings and hydrocarbon packing the overall morphology is also diverse for the Zn-Al LDHs synthesized with different amounts of SDS which is clear in the SEM micrographs presented in Figure 2.13. Besides hexagonal platelets of 2-3 μm (no SDS) and hollow rings of 35-50 nm (100 mM SDS), coral-like and ‘pompon-like spherical morphology composed of curved, intercrossed sheets’ that were reported before were also observed for 5 mM and 15 mM SDS, respectively.^{20, 91, 92, 100, 103} Li and He argued that the morphology of the Mg-Al LDH platelets could be changed by using SDS at a concentration higher than the anion exchange capacity (AEC) yet the morphology diversified when [SDS] increased more (the study was summarized in Table 2.5).^{100, 103} They observed coral like morphology by using SDS at an amount 1.75 times of AEC and the curvature increased with [SDS] =2 AEC. In this study we observed even [SDS] =AEC was enough to influence the structure of the particles to obtain coral-like morphology.

It is discussed in section 2.2.1 that the urea hydrolysis method give rise to a two-step process where Al hydroxide is formed first and LDH grow around this Al seed later. This two-step mechanism is also verified for SDS-intercalated LDH by B.Li *et al.*¹⁰⁰ They observed Al hydroxide is formed in 1h and characteristics of SDS intercalated LDH appear at prolonged times but disappear after 120h indicating surfactant exclusion through ion-exchange with CO_3 even though the bent morphology does not change. However, when we increased reflux time to 120h despite the loss of crystallinity to some degree and perfect layer stacking, basal spacings characteristic to the SDS intercalated LDH were still present

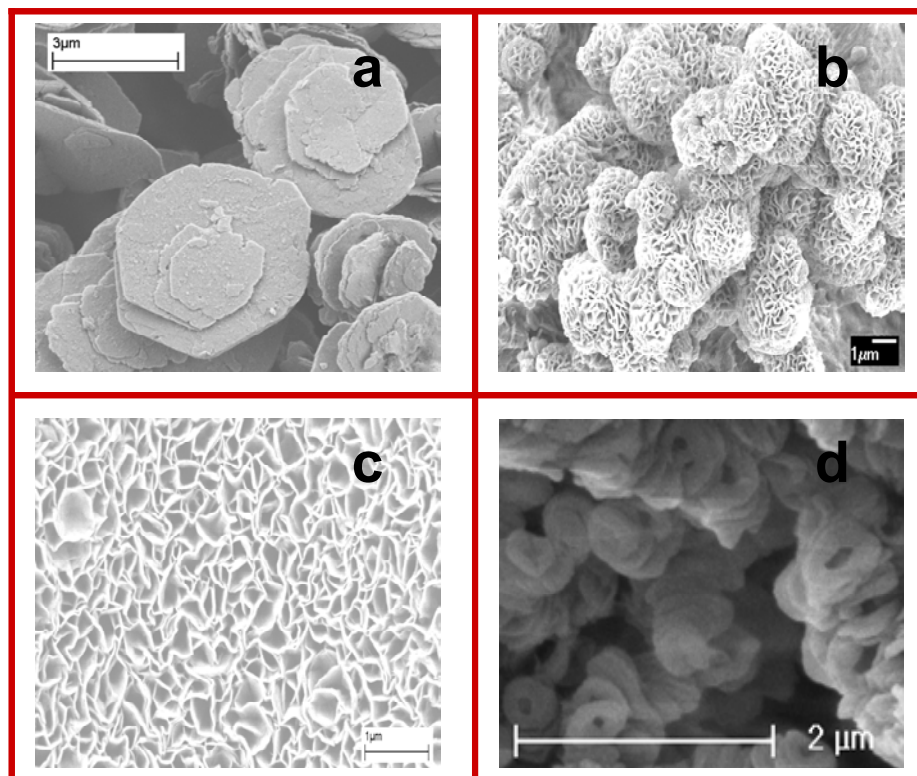


Figure 2.11 SEM images of Zn-Al LDH synthesized in the presence of a) no SDS. b) 5 mM SDS. c) 15 mM SDS. d) 100 mM SDS.

(Figure 2.10 and Table 2.4) with an increase for the 100 mM sample. Characteristic CO_3 -LDH reflections were not observed despite of the occurrence of a few hexagonal platelets. There was an increase in the particle size but the overall morphology was preserved (Figure 2.14). This increase in the lateral size with time suggests crystal growth is preferential along ab plane. Furthermore, the decrease in the size along c from 1.404 for CO_3 -LDH to 6.321 for SDS-LDH (100 mM, 24h) favors the view that presence of SDS inhibits the growth in the c direction.

Table 2.5 Change in the morphology of the Mg-Al LDH with SDS concentration by Li and He¹⁰⁰

[SDS] (mM) AEC		[Mg ²⁺] (mM)	[Al ³⁺] (mM)	Morphology
10	1	20	10	Sand-Rose Aggregates
15	1.5	20	20	Sand-Rose Aggregates
17.5	1.75	20	10	Sheet-Curved / Bended
20	2	20	10	Sheet-Curved / Bended with increased curvature

The hollow-rings were obtained in 100 mM SDS which corresponds to 20 times of the AEC. The concentration of SDS used in this synthesis is above both the 1st and 2nd CMC (8.3 mM and 65 mM, respectively). It is already stated in section 2 that addition of salt lowers both CMCs and also triggers the transformation from a spherical micelle into a cylindrical one assuming it was still spherical above 2nd CMC. Li and He suggest vesicles of SDS at room temperature form when 20 mM Mg²⁺ and 10 mM Al³⁺ were added on 15 mM SDS which are used for the template-mediated synthesis.¹⁰³ They were expecting to obtain curved or spherical morphology and observed bent particles. The dependence of the

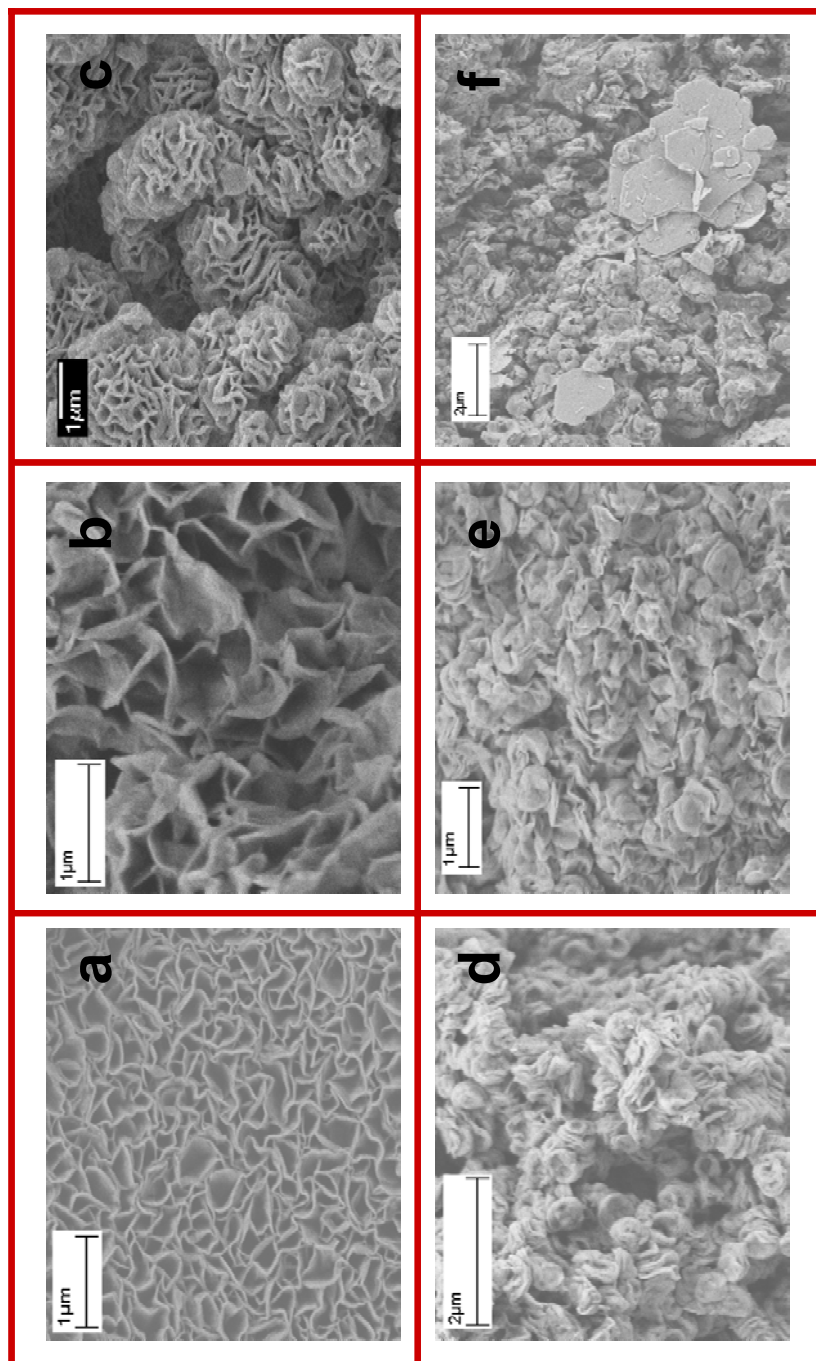


Figure 2.12 SEM micrographs of the Zn-Al LDHs synthesized in the presence of different SDS concentrations for varying times. a) 15 mM SDS, 24h. b) 15 mM SDS, 72h. c) 5 mM SDS, 24h. d) 100 mM SDS, 24h. e) 100 mM SDS, 72h. f) 100 mM SDS, 120h.

morphology on [SDS] was related to the absence or presence of free vesicles that are not intercalated. They propose at high concentrations only part of the surfactants is intercalated and LDH particles grow on the vesicles formed by the rest of SDS. But at low concentrations most of the surfactant is intercalated and LDH particles grow into platelets (Figure 2.15). At 100 mM SDS concentration, it is possible that enough SDS is available for intercalation and vesicles are maintained for a prolonged time causing ring morphology. However, this theory alone still does not account for the formation of the hollow-rings of LDH particles. Detailed phase analysis of the surfactant under the synthesis conditions; at the reflux temperature with / without urea is needed for a plausible explanation.

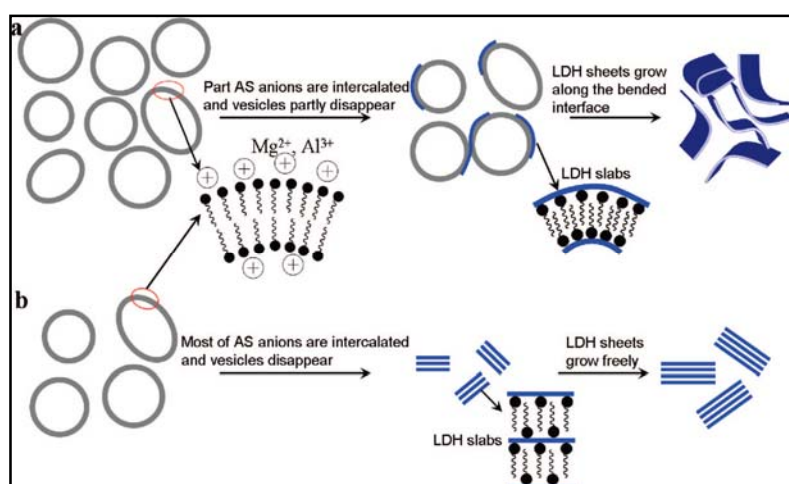


Figure 2.13 Proposed scheme for the formation of curved LDH.¹⁰³

The coral-like morphology was also observed when the LDH was synthesized in the presence of a zinc plate under identical conditions with 15 mM SDS experiment. Although it seems like the spheres of curved sheets were hidden under a smoother film, water droplets failed to wet the surface of the plate (Figure 2.16).

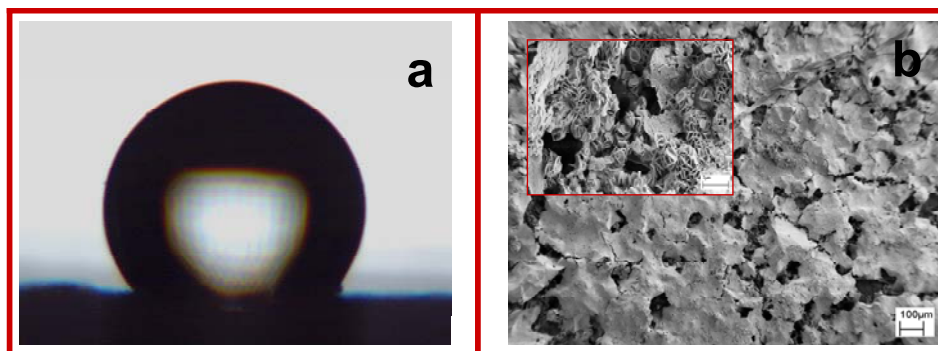
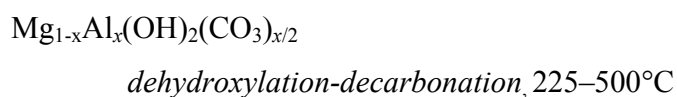
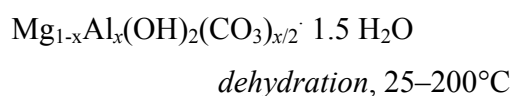


Figure 2.14 Hydrophobicity of the Zn-Al LDH synthesized in the presence of zinc plate and 15 mM SDS. a) Dewetting surface of the zinc plate. b) SEM image of the zinc plate.

Thermogravimetric curves obtained for the CO_3 -LDH and SDS-LDHs synthesized by using different amounts of SDS are shown in Figure 2.10. In all compounds three major mass-loss steps are observed. These consecutive events are commonly attributed to the loss of interlayer and physisorbed water, dehydroxylation and a combination of dehydroxylation-decarbonation reactions respectively as shown in scheme 2.1, although Kanezaki *et al.*¹⁰⁷ proposed decarbonation occurs before dehydration takes place through a chemical reaction between the intercalated carbonates and the water.^{101, 108, 109}



The nature of the dehydroxylation- decarbonation step is proposed to depend on the $\text{Mg}^{2+}/\text{Al}^{3+}$ ratio.¹¹⁰ Zhao et al observes the dehydroxylation-decarbonation step as two different processes at $\text{Mg}^{2+}/\text{Al}^{3+} = 2$; first partial loss of OH^- occurs and it is followed by the complete loss of OH^- and carbonate anions. On the contrary, there are reports claiming decarbonation starts as early as 227°C ¹¹¹ and even occurs between $80^\circ\text{C} - 230^\circ\text{C}$.¹¹² For most LDHs, the structure decomposes at higher temperatures and the residue remains above 500°C is generally attributed to be divalent metal oxides ($\text{M}^{\text{II}}\text{O}$, $\text{M}_2^{\text{III}}\text{O}_3$) and/or the mixed metal spinel ($\text{M}^{\text{II}}\text{M}^{\text{III}}\text{O}_4$).¹¹³

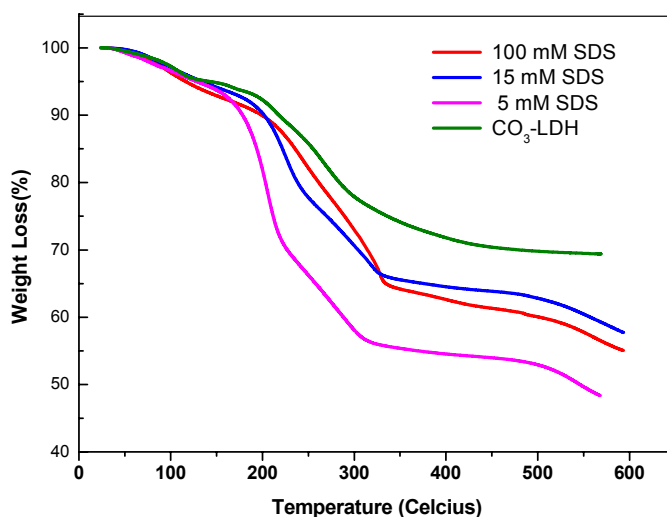


Figure 2. 15 Thermogravimetric mass loss (TG) curves for LDH- CO_3 and SDS intercalated LDH.

In all compounds shown in Figure 2.17, the first weight loss step is observed to be finished up to about 200°C and indicates similar water content for SDS intercalated samples (around 5% for LDH- CO_3 and 9% for LDH-SDS). The second decomposition step shows differences in the modified samples typical for SDS intercalated LDH.⁹⁴ The greater

weight loss suggests lower thermal stability for all the SDS modified samples with no clear indication of a trend depending on the surfactant molarity (summarized in Table 2.6). The decomposition of dodecyl sulfate ions observed in between 210-250°C (Leroux, 2001). LDHs synthesized in the presence of 100 mM and 15 mM SDS seems to intercalate similar amounts of organic content whereas the one synthesized with 5 mM SDS 1 ca. of the anion exchange capacity (AEC) shows lower amount of surfactant in its structure.

Table 2.6 TGA reports of the LDH-CO₃ and LDH-SDS

System	%wt loss at 200°C	%wt loss at 400°C	%wt loss at 500°C
LDH- CO ₃	92.27	71.79	62.79
LDH-SDS (5 mM SDS)	81.90	54.54	52.93
LDH-SDS (15 mM SDS)	90.28	64.52	62.80
LDH-SDS (100 mM SDS)	89.93	62.17	60.05

2.2.3 Effects of Sodium Laurate on the Morphology of Zn-Al LDHs

Curved morphologies observed with SDS can be also found in the literature. It was reported before that dodecyl sulfate, dodecyl sulfonate, bis(2-ethylhexyl) sulfosuccinate induced similar curved morphology when they were used in higher amounts than AEC and at concentrations around 20 mM.¹⁰⁰ The same phenomenon was also observed in another study with dodecyl sulfate, dodecyl benzene sulfonate, laurate, bis(2-ethylhexyl)hydrogenphosphate.⁹⁴ To investigate the dependence of the curved and especially the ring morphology of LDHs that we have observed with SDS on the surfactant type, sodium laurate was used to synthesize surfactant intercalated Zn-Al LDH. Influences

of the initial Zn/Al ratio and surfactant concentration were explored (The synthesis conditions are summarized in Table 2.7).

Table 2.7 Synthesis parameters of SL intercalated Zn-Al LDH

Sample	[SL] (mM)	[Zn ²⁺] (mM)	[Al ³⁺] (mM)
SL-1	100	10	10
SL-2	100	10	5
SL-3	100	10	2.5
SL-4	100	10	0.5
SL-5	100	10	-
SL-6	15	10	5

Raman and FT-IR spectroscopy verify the presence of the surfactant in the final powders. In Figure 2.18, two different parts of Raman spectrum of SL-2 are displayed; 3100-2600 cm⁻¹ region and 1600-650 cm⁻¹ region. Bands at 2845, 2880, and 2963 cm⁻¹ can be assigned to CH₂ symmetric, CH₂ asymmetric, CH₃ asymmetric stretching vibrations, respectively. The CH₃ symmetric stretching band appears very clearly in the spectra of myristic acid and sodium myristate (CH₃(CH₂)₁₂COOH) is not observed.¹⁰² The bands at 1460 and 1439 cm⁻¹ are due to CH₂ scissoring mode in the second region. The bands at 1127 and 1061 cm⁻¹ are due to the C-C stretchings are attributed to the all-trans conformation of the alkyl carboxylate by Borja and Dutta.¹⁰² The band at 890 cm⁻¹ accounts for the methyl rocking mode.

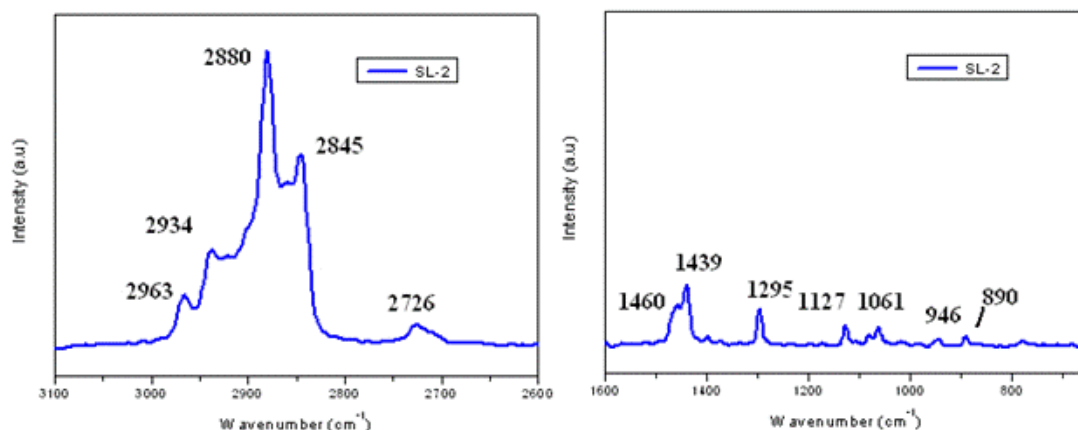


Figure 2.16 Raman spectrum of SL-2; 3100-2600 cm^{-1} region on the left and 1600-600 cm^{-1} region on the right.

The FT-IR spectra for sodium laurate, lauric acid and the laurate intercalated LDH powdery composites are compared in Figure 2.19. The C-H stretching region (3100-2500 cm^{-1}) of the spectra coincide with each other except in the case of lauric acid the peak is very broad. The characteristic $-\text{CH}_2$ stretching bands were observed at 2955, 2916 and 2849 cm^{-1} and the $-\text{CH}_2$ bending peaks were at 1468 cm^{-1} . The broad band between 1719-1681 cm^{-1} in the lauric acid spectrum is the characteristic stretching band of the carbonyl group. The asymmetric stretching of the carbonyl appears at 1555 cm^{-1} in sodium laurate. Four bands are observed in the carbonyl stretching region for the SL1-6 compounds at 1624, 1596, 1544(ν_{sym}) and 1412 cm^{-1} (ν_{asy}). Borja and Dutta discuss that the appearance of the bands around 1590 and 1640 cm^{-1} suggest the presence of RCOOH form of the surfactant inside the layered compounds.¹⁰² The progression of the bands in the CH_2 wagging region,(1350-1150 cm^{-1}) is attributed to the all-trans conformation of the alkyl chains in accordance with the Raman data.¹⁰²

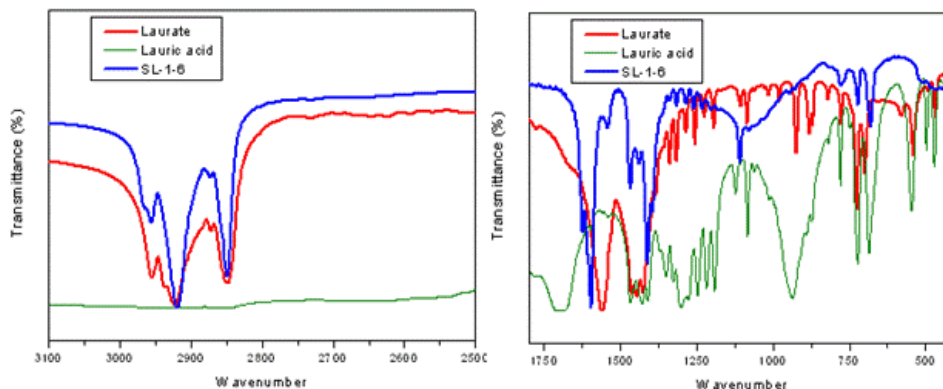


Figure 2.17 FT-IR Spectra of lauric acid, laurate and SL-1;6.

Thermal behavior of the laurate modified samples are very similar to LDH-laurate and LDH-stearate thermal decomposition reported in the literature showing a greater mass loss than the non-intercalated Zn-Al LDH except the dehydration step as shown in Figure 2.20.^{94, 102, 106, 114} Dehydration step which generally occurs up to 200°C is not observed for the compounds synthesized in the presence of 100 mM SL. The decomposition of the surfactant anions start around 250°C in the sample with no Al and it is shifted to 350-400°C for the sample with $\text{Zn}^{2+}/\text{Al}^{3+}=2$ which is consistent with fatty acid intercalated LDH.

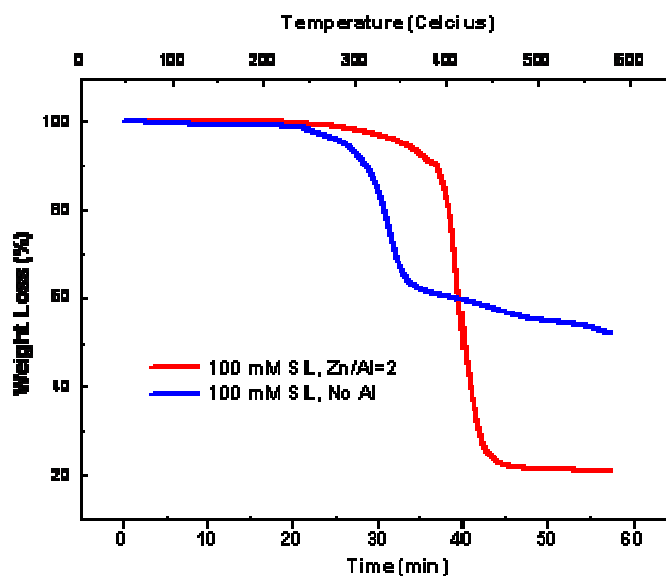


Figure 2.18 Thermogravimetric mass loss (TG) curves for SL-2 (Zn/Al=2) and SL-5 (No Al).

The XRD profiles of the synthesized materials demonstrate the formation of layered compounds with characteristics of laurate intercalation in all cases (Figure 2.21). A series of sharp and intense reflection signals almost equally spaced at low angles accompanied with higher order reflection peaks are observed. Both the diffraction pattern and the d spacing values of SL-2 and SL-5 are very similar that is reported for laurate intercalated Mg_2Al LDH ($d=3.5 \text{ nm}^{102}$ and 3.66 nm^{87}) and other alkyl carboxylate intercalated LDHs.^{106, 114} However, the basal spacing of 2.92 nm for SL-1 is very close to 2.94 nm observed for zinc laurate.^{30, 115} When the XRD profiles of the sodium laurate and SL-1 are compared, it is seen that the reflection peaks of the sodium laurate do not suggest regularly repeated structure as that of SL-1 in Figure 2.22.

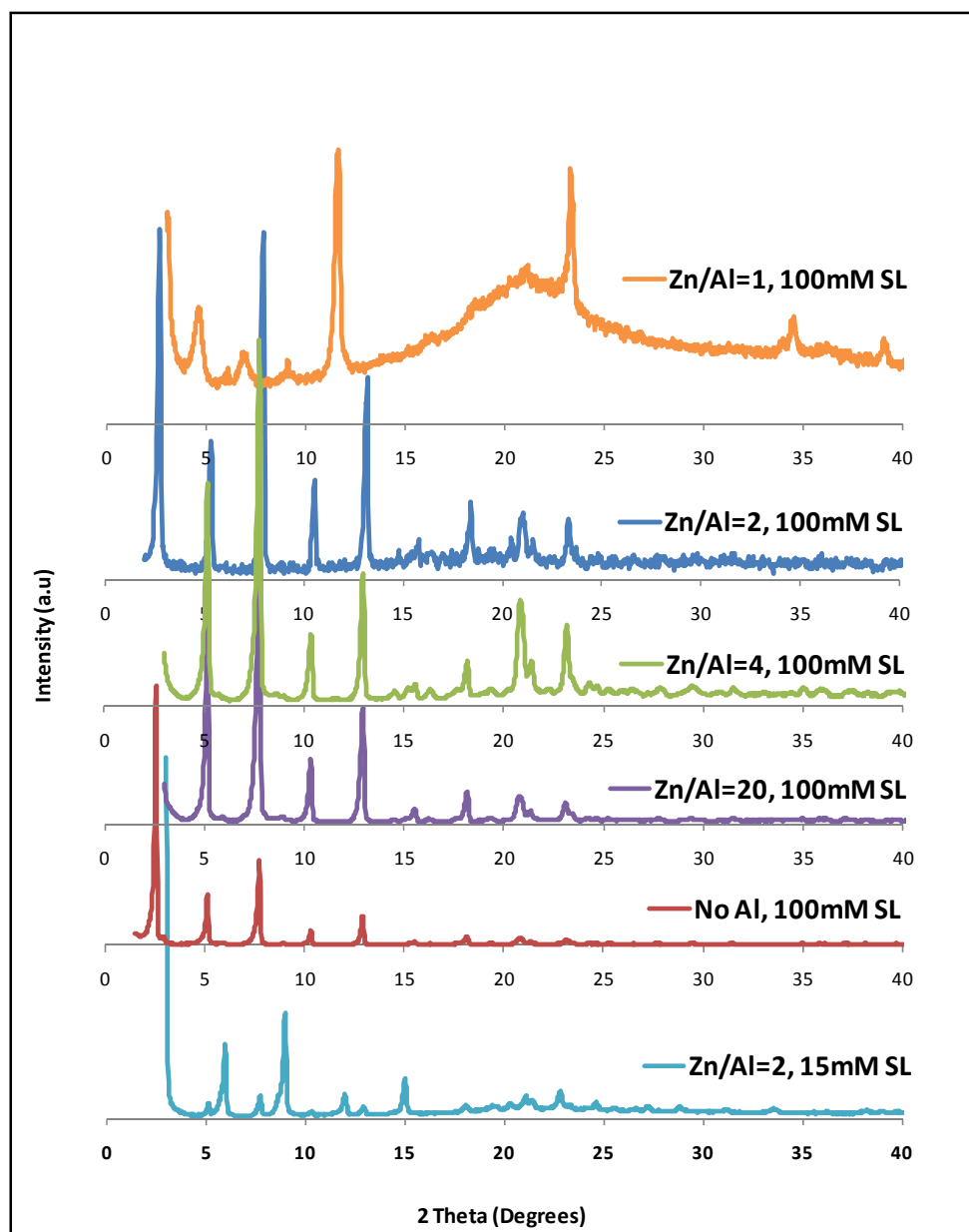


Figure 2.19 XRD Profiles of SL-1 (Zn/Al=1, 100 mM SL), SL-2 (Zn/Al=2, 100 mM SL), SL-3 (Zn/Al=4, 100 mM SL), SL-4 (Zn/Al=20, 100 mM SL), SL-5 (No Al, 100 mM SL) and SL-6 (Zn/Al=2, 15 mM SL).

Table 2.8 Interlayer distances of the Layered Hybrids

Sample	[SL] (mM)	Zn / Al	<i>d</i> (nm)
SL-1	100	1	2.92
SL-2	100	2	3.20
SL-3	100	4	2.44
SL-4	100	20	2.76
SL-5	100	No Al	3.47
SL-6	15	2	2.48

When surfactant concentration was 15 mM (SL-4) the regularity of the pattern and high degree of crystallinity are lost and characteristic peaks of the CO₃-LDH appear at 2θ values of 11.66° and 21.32° indicating mixed phase (Figure 2.21). The *d* spacings of the SL-compounds slightly differ from each other. N. Iyi *et al.* suggest the peak corresponding to *d*=2.399 nm belongs to the main phase and *d*=3.78 nm to the ‘secondary phase’ for Mg-Al LDH-laurate synthesized with ammonia releasing reagent which disappears after hot EtOH wash.⁹⁷

N. Iyi *et al.* argues interdigitated monolayer arrangement with an angle of 62° to the basal plane for the main phase and tilted-bilayer arrangement of the carboxylates with an angle of 67° for the secondary phase assuming the long axis length of laurate as 1.78 nm. In another study of the long chain carboxylates, Itoh *et al.* found a relation between the layer spacing of $001(d)$ and the number of carbons in the aliphatic chain(*n*) as $d(\text{nm}) = 0.85 + 0.2454n$ and also suggests bilayer arrangement with a tilt angle of 61° to the basal plane.¹⁰⁶ Based on this relation the d_{001} should be 3.55 nm which is still close to 3.20 (SL-2) and 3.47 nm (SL-5). The packing of the alkyl carboxylates in between the LDH layers has also created sometimes controversial and sometimes supporting explanations.

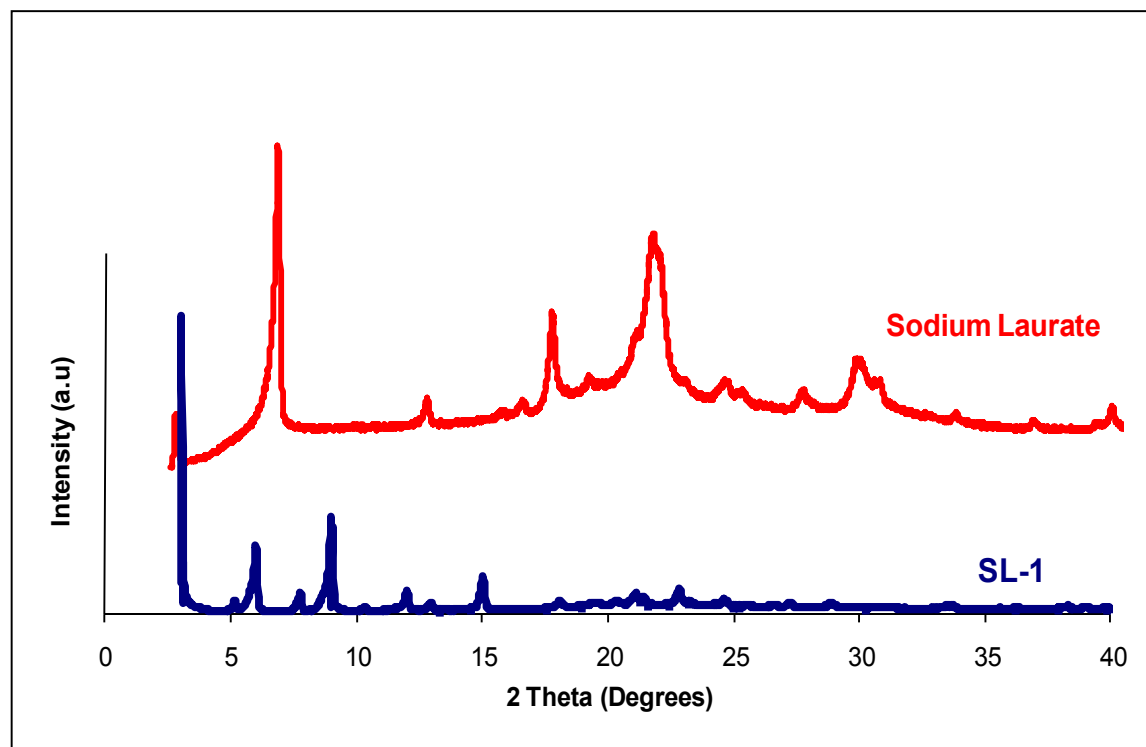


Figure 2.20 Comparison of the XRD patterns of SL-1 with that of sodium laurate.

Meyn *et al.* proposes the relation between interlayer distance of the alkyl carboxylate and the arrangement of the carboxylate in the interlayer gallery of the LDHs represented by Eqn.2.5.¹⁰⁴ Tilted monolayer of interdigitated carboxylates in their fully extended states are suggested by Xu and Braterman.¹¹⁶ They calculated d spacing with an equation stated before (Equation 2.8.) and found $\theta=55^\circ$ for the ideal case where carboxylate oxygens interacted with the metal layer equally. However, for LDH-palmitate, LDH-stearate and LDH-elaidate when excess anions are present, they have observed XRD reflections that can be attributed to the bilayer packing mode with an ideal angle of 55° that is expressed in Equation 2.9. Then, in the ideal case d should be 3.61 nm which is slightly higher than 3.20 (SL-2) and 3.47 nm (SL-5).

$d = 1.25 + 0.13 (n-2)\sin\theta$, where n is the carbon number in the molecule and θ is the tilt angle. (Eqn. 2.8)

$d = 1.48 + 0.26 (n-2)\sin\theta$, where n is the carbon number in the molecule and θ is the tilt angle (Eqn 2.9)

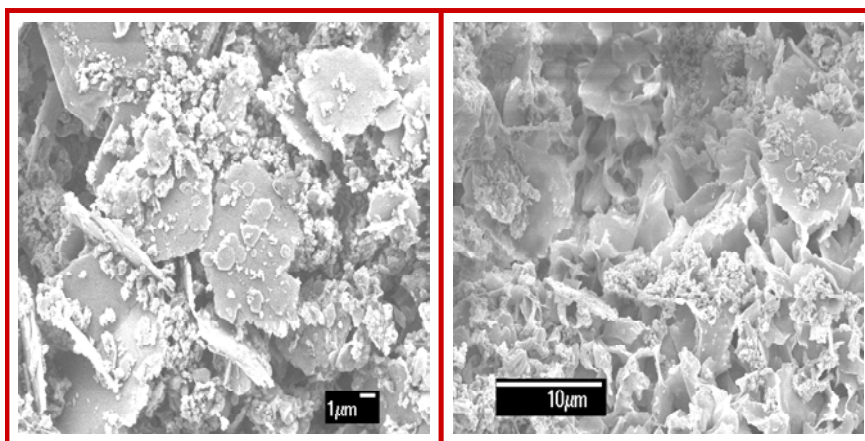


Figure 2.21 SEM micrographs of SL-6 (15mM SL and $\text{Zn}^{2+}/\text{Al}^{3+}=2$) before (left) and after (right) hot EtOH wash.

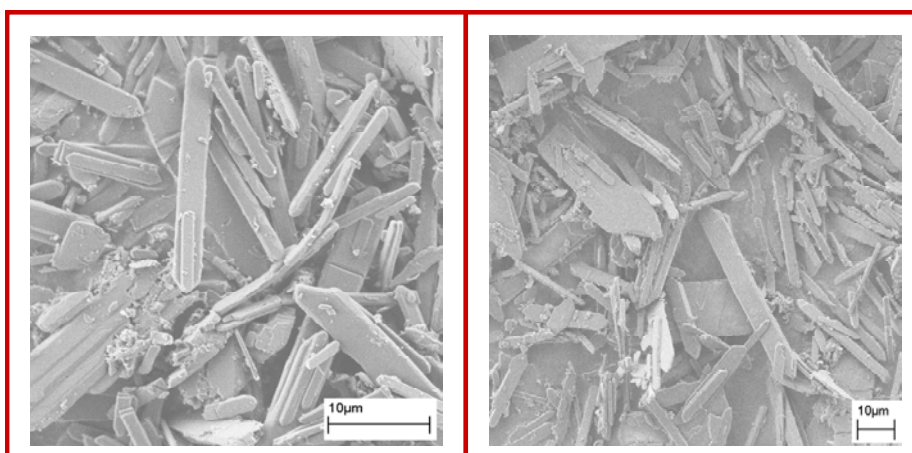


Figure 2.22 SEM images of SL-2 (SL=100mM at 90°C) for 24 h(left) and for 72h (right).

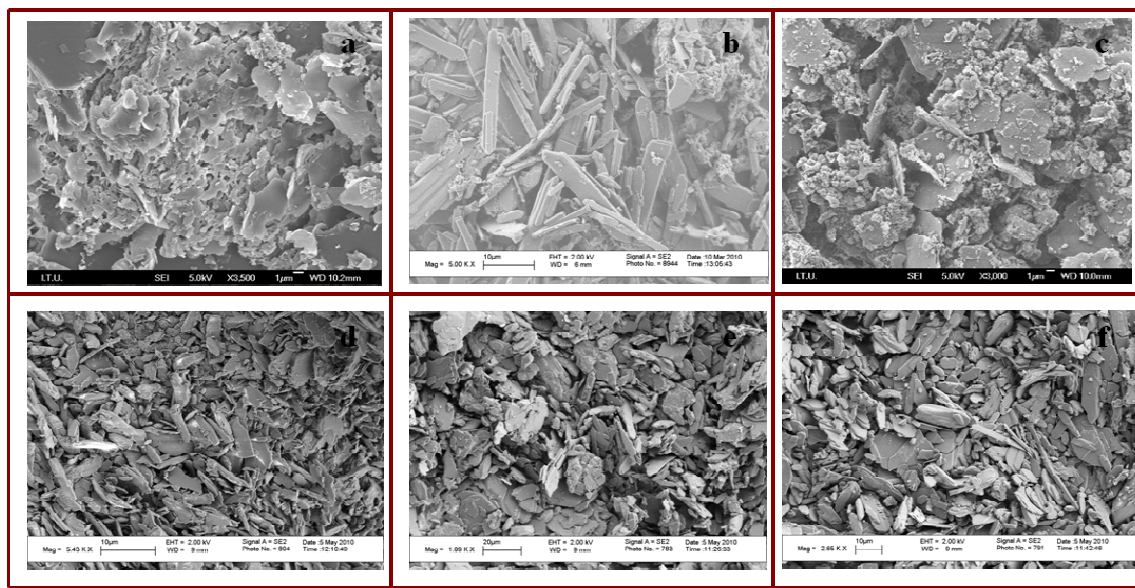


Figure 2.23 SEM images of the layered ZnO platelets. a. SL-1 (Zn/Al=1, SL=100 Mm). b. SL-2 (Zn/Al=2, SL=100 Mm). c. SL-6 (Zn/Al=2, SL=15 Mm). d. SL-3 (Zn/Al=4, SL=100 Mm). e. SL-4 (Zn/Al=20, SL=100 Mm). f. SL-5 (No Al, SL=100 Mm).

When the SEM images of the compounds are examined (Figure 2.25), besides varying among each other a completely different morphology from both conventional and ring-curved shaped LDHs were observed. Mostly stacked plates with a very high aspect ratio have been formed except for SL-6. When the SL concentration was lower than CMC (26 mM), the structures resemble rounded plate of low aspect ratio. They form cavities after hot ETOH wash (Figure 2.23). Increase in the SL concentration induces the formation of rod-like particles with tapered tips. When Zn/Al=1 (SL-1), the structures are irregular and larger in width. Decreasing Al concentration to half (SL-2, Zn/Al=2) result in the most ordered particles with 10-60 μm size in length around 2.5-10 μm in width. Increase in the reaction time results in the enlargement of the particles (Figure 2.24). At Zn/Al=4 (SL-3), both length and aspect ratio are reduced. Upon increasing Zn/Al ratio further to 20 (SL-5), reduces the aspect ratio even more and wider particles are obtained. Finally eliminating Al

completely from the synthesis mixture does not induce a significant change in the morphology (SL-6). This surprising result is consistent with the coinciding XRD profiles. The fact that the similar structures are formed even without Al indicates the Zn-Al layered double hydroxide is not obtained. More interestingly the EDX analysis revealed that even when Al is present in the medium (Zn(Al=2, SL-2), it is excluded from the particles. There are two plausible explanations; laurate intercalated zinc hydroxide formation¹¹⁷⁻¹¹⁹ or formation of layered zinc oxide particles²⁷.

Table 2.9 EDX Results of SL-2

Element	at. %	Error in [%]
Aluminium	0.59	0.38
Zinc	4.66	8.79
Oxygen	94.76	9.70

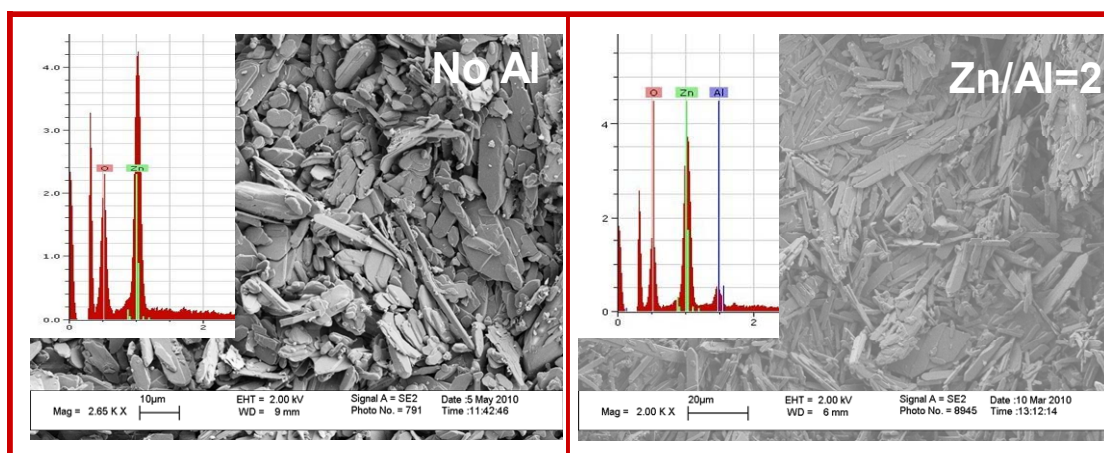


Figure 2.24 SEM images of samples with and without Al^{3+} (SL-5 on the left and SL-2 on the right). EDX patterns are shown in the inlets.

The UV-Vis absorption spectra of the compounds (Figure 2.27) show absorption onsets of 381 nm for SL-4 and 368 nm SL-1, SL-2, and SL-5 which are lower than the typical onset observed for ZnO nanoparticles, 390 nm.^{27, 120} The absorbance peaks at around 430 nm and 600 nm detected for all samples might be consistent with observation of the wide absorption of a commercial ZnO by Zhao *et al.*¹²¹ However, samples are not luminescent under UV/vis light. This aforementioned results together with the absence of a melting event at around 131°C (melting point of zinc laurate soap¹¹⁵) eliminates the soap and ZnO formation. Hence, taking into account that the same structure is formed even in the absence of Al, we propose laurate intercalated layered zinc hydroxide formation. Zn(OH)₂ is a brucite-like material where the OH⁻ ions are hexagonally close-packed and the Zn²⁺ ions reside in the alternate layers of octahedral sites.¹²⁰ The basal spacings and XRD pattern are very close to SDS intercalated zinc hydroxide.¹¹⁷

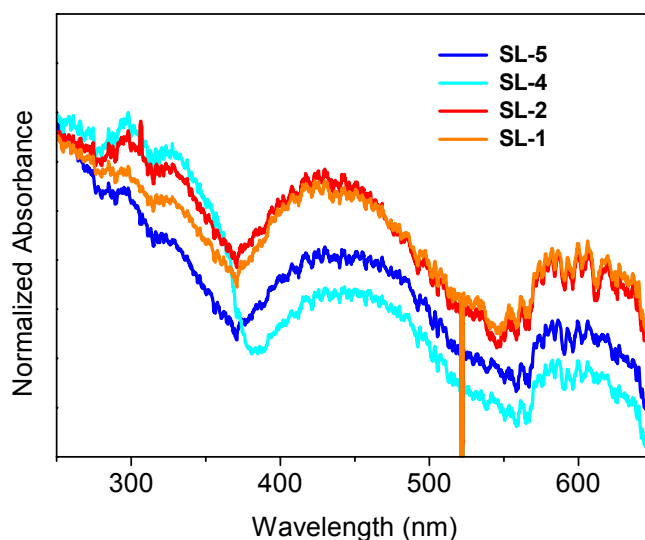


Figure 2.25 UV-vis absorbance spectra of SL-1, SL-2, SL-3, SL-4 and SL-5.

In addition, the rod-like morphology observed can be explained by the growth habit of the hydroxide crystals.⁵² First of all, abundant with oxygens *c*-axis of the crystal is more polar and it is stabilized by the laurate ions in solution. As W.J. Li *et al.* explains, the coordination polyhedron has a face at the interface in the (0001) direction so slowest growth occurs through this direction and fastest growth occur in the (0100) direction where coordination polyhedron has a corner (Figure 2.28).

The difference both in morphology and structure created by the two surfactants can be explained by the different interactions of the functional groups with the metals. Carboxyl group is a hard base and Al is a hard acid whereas sulfate group and zinc are borderline materials. In the case of SDS intercalation, Al(OH)₃ precipitates first at low pH as a nucleation site and zinc interacts with the SDS micelles or vesicles. Thus growth occurs through the micelles/vesicles around the Al(OH)₃ which later dissolves at higher pHs around 8.3-8.5 giving rise to rings of Zn-Al LDH. The situation is different with laurate. Laurate may form complexes preferentially with Al hence prevents the precipitation of Al(OH)₃ which would form the nucleation sites for LDH growth. Remaining surfactant interacts with zinc and zinc hydroxide is formed which will not dissolve until pH 12-14.¹²² Since the solubility of aluminum laurate in water is very low⁵⁸, it will be excluded from the structure. Besides as explained earlier, there is a high chance that SDS forms spherical micelles and laurate forms cylindrical ones. At high concentrations these micellar forms are probably acting as a template and influence the morphology.

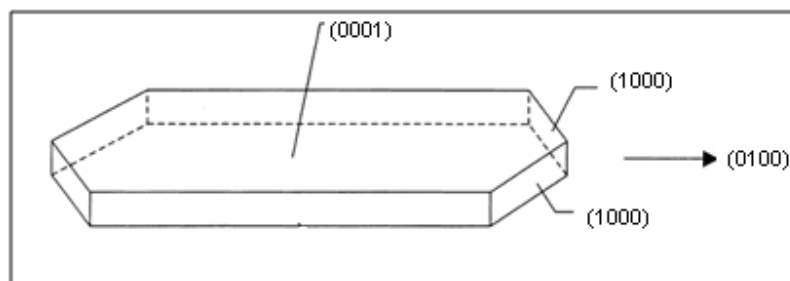


Figure 2.26 Schematic representation of growth habit of hydroxide crystals.

2.3 Conclusions and Prospects

Influence of the SDS and SL on the formation and morphology of Zn-Al layered double hydroxides were examined. The structure and the morphology induced by the two surfactants were different. For the SDS case, when the surfactant used in low concentrations (5 mM / 15 mM) meaning at or slightly above the AEC, coral-like morphology was obtained in accordance with the reported cases of Mg-Al or Ni-Al. The use of SDS below or above the CMC did not play a critical role at these concentrations. When SDS amount was 20 times of the AEC, Zn-Al LDH with ring morphology was obtained for the first time. We conclude that 5 to 15 mM of the surfactant is used for the intercalation while the excess has a templating role in the growth.

When SL is used either above or below CMC, layered zinc hydroxide with rod-like morphology rather than LDH was formed which is attributed to the preferential interaction of the aluminum and laurate.

Future investigations should be concentrated on the solubility of the ligand-metal complexes and shape of the micelles. A detailed study on the shape of the surfactant micelles in the presence of zinc, aluminum and urea at 90°C is needed to understand the

path leading to the ring formation. The studies on the solubility and the stability of the zinc-laurate, zinc-dodecyl sulfate, aluminum laurate, aluminum-dodecyl sulfate in the pH range 2.5 and 8.5 will be important for the explanation of the zinc hydroxide formation with laurate. In addition zinc oxide, a II-VI semiconductor has attaining interest in science and technology world due to its applicability to many systems. It might be possible to obtain luminescent ZnO particles with ring or rod morphology through the calcinations of the obtained LDH-products. Furthermore, ZnS QDs in the lamellar structure may be obtained by reacting the layered zinc hydroxides with sulfur sources.

Chapter 3

SYNTHESIS OF LAYERED DOUBLE HYDROXIDES/ QUANTUM DOT HYBRID SYSTEMS

Excellent biocompatibility of LDHs combined with unique optical properties of QDs makes LDH/QDhybrids very interesting and valuable materials for many but especially bio-applications where delivery and imaging is desired at the same time with the same material.

The luminescence intensity of the ODs decreases with time though they are more stable than organic flurophores.⁶⁴ It is known that surface defects that can be attributed to $\text{Cd}^{2+}/\text{Te}^{2+}$ and S^{2-} vacancies or dangling bonds cause decrease in the luminesncese intensity by acting as nonradiative recombination centers.^{44, 123, 124} These particles suffer from instability when exposed to light and air. It has been shown that the luminescence properties can be enhanced by surface passivization with organic molecules⁷², forming an lower band gap-energy semiconductor shell⁷³ or a inorganic $\text{Cd}(\text{OH})_2$ shell ⁷⁴around the core QD. Hence we want to see whether being inside the LDH galleries would enhance the optical properties of the QDs and their stability.

There have been a few studies reported of LDH/QD hybrid structures. Only a few of them discuss the changes in the luminescence characteristic of the nanoparticles. One of the methods used to create such hybrids is to exchange NO_3^{2-} anions in between the metal

layers with precursor complexes to yield the nanoparticles later. In one of the studies, ZnS nanoparticles have been obtained by exchanging NO_3^{2-} anions with $\{[\text{Zn}(\text{Cit})]^{2-}\}$ complexes ($\text{Cit} = \text{C}_6\text{H}_4\text{O}_7^{4-}$) and reacting the resulting material with H_2S gas.¹²⁵ The same method was also used to synthesize CdS QDs inside mesoporous MCM-41.¹²⁶ Han *et al.* prepared CdS/montmorillonite nanocomposites through hydrothermal decomposition of $\text{Cd}[\text{NH}_2\text{CSNH}_2]_2$ complex inside the clay galleries.¹²⁷ They detected an increase in the basal spacing with the amount of the complex for the exchange reaction. However, after a certain limit, hexagonal nanocrystal formation and agglomeration outside the interlayer are observed. Lukashin *et al.* reported synthesis of PbS nanocrystals inside Mg-Al LDH through UV irradiation and thermal treatment of thiosulfate complex $[\text{Pb}(\text{S}_2\text{O}_3)_2]^{2-}$ that was exchanged with the NO_3 anions inside the gallery.¹²⁸ In another study the same group synthesized PbS-LDH hybrid through reversible delamination of MgAl-LDH.¹²⁹ They observed higher quantum yield (QY) for the composite materials 8.2% than the starting QD solution (4.5%). The enhancement in the QY however is attributed to the ‘extra absorption of the exciting radiation by LDH and further energy transfer to the QDs’. A similar delamination/restacking method was used by Venugopal *et al.* They introduced pre-prepared CdSe QDs during restacking of the delaminated layers of Mg-Al-SDS.¹³⁰ A different strategy was developed by Guo *et al.* They synthesized SDS intercalated $\text{Cd}(\text{OH})_2$ and Cd-Al LDH and form CdS nanocrystals implanted on the matrices by reacting these materials with H_2S .¹³¹ In addition composite multilayer films were formed by layer by layer deposition of anionic CdS QDs and LDHs.¹³² A monolayer film of the particles on LDH without coalescence has been observed. Luminescent composite materials were also achieved by intercalating anionic Europium(III) complexes in Zn-Al LDH.¹³³

3.1 Experimental

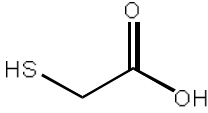
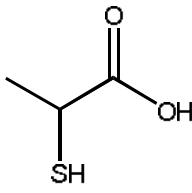
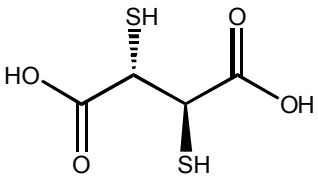
3.1.1 Materials

All chemicals were analytical grade or of the highest purity available and used without further purification. Sodium sulfide trihydrate ($\text{Na}_2\text{S}\cdot 3\text{H}_2\text{O}$), 3-mercaptopropionic acid ($\text{HSCH}_2\text{CH}_2\text{COOH}$, 3-MPA), 2-mercaptopropionic acid (HSCH_2COOH , 2-MPA), cadmium acetate dihydrate ($\text{Cd}(\text{CH}_3\text{COO})_2\cdot 2\text{H}_2\text{O}$), cadmium nitrate tetrahydrate ($\text{Cd}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$), HNO_3 (65 %), sodium nitrate (NaNO_3) and aluminum nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$) were purchased from Merck. Sodium hydroxide, Polyacrylic acid sodium salt (PAA, 5100 g/mol) and zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$) were purchased from Aldrich and LaCheMa, respectively. Magnesium nitrate hexahydrate ($\text{Mg}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$) and meso-2,3-dimercaptosuccinic acid (DMSA, $\text{C}_4\text{H}_6\text{O}_4\text{S}_2$) were purchased from Sigma and Fluka respectively. Na_2Te was synthesized by Selçuk Acar (Inorganic Chemistry Lab, KU) from sodium and tellurium in liquid NH_3 as previously reported.⁵⁷ Milli-Q water was used in all procedures. The chemical structures of the ligands used for the synthesis are provided in Table 3.1.

3.1.2 Anion Exchange Reactions of Zn-Al-SDS

The interlayer SDS anions of the Zn-Al-LDH described in chapter 2 were replaced to incorporate QDs to the LDH. Two different strategies were used to achieve this goal. The first one is to exchange SDS with pre-made QDs and the other one is to synthesize QDs in the intergallery after exchanging SDS with Cd:ligand complexes. CdS-2-MPA and CdS/CdTe QDs were synthesized for the exchange reactions as described in the following sections.

Table 3.1 Chemical structures of the ligands used in the QD synthesis

Chemical Name	Structure
3-MPA	
2-MPA	
DMSA	

3.1.2.1 Anion Exchange of Zn-Al-SDS with prepared CdS and CdTe/CdS Core/Shell QDs

SDS-LDH was dispersed in decarbonated distilled water. Pre-prepared QDs, CdS-2MPA, CdTe-2MPA or CdTe/CdS (described in the following section) was also dissolved in decarbonated water and mixed with SDS-LDH in Cd:LDH 1:1 w/w ratio under Argon. The mixture was stirred with a mechanical stirrer overnight. Composite structures were recovered by centrifugation at 3900rpm for 30 min and washed with decarbonated water four times.

a. Synthesis of 2-MPA Coated CdS QDs

2-MPA coated CdS QDs were prepared using a similar procedure as reported before.⁶⁰ All the steps were performed under Argon. Briefly, 66.6mg of $\text{Cd}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ was dissolved in 50ml of water in a 250-ml four-necked round bottomed flask fitted with a mechanical stirrer. After addition of 44 μl 2- MPA, pH of the solution was adjusted to 7.5 with 10M NaOH and/or concentrated acetic acid. The sulfide solution was prepared by dissolving 13.2 mg of $\text{Na}_2\text{S} \cdot 3\text{H}_2\text{O}$ in 50 ml of water in an ultrasonication bath. Following deoxygenation the sulfide solution was added to the cadmium-MPA solution through an addition funnel. Reactions were carried out for 40 min.

b. Synthesis of CdTe and CdTe/CdS Core/Shell QDs

CdTe/CdS Core/Shell QDs were prepared using a similar procedure as reported before.⁶¹ All the steps were performed under Argon. Briefly, 213.2 mg of $\text{Cd}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ and 161 μl 2-MPA were dissolved in 160 ml of water in a 250-ml four-necked round bottomed flask fitted with a mechanical stirrer. The pH of the solution was adjusted to 7.5 with 10M NaOH and/or concentrated acetic acid. 53 mg Na_2Te was weighed into a round bottom flask in the glow box (O_2 and H_2O below 1 ppm) and the flask was sealed before being expelled to air. Upon transfer of 20 ml of deaerated distilled water on Na_2Te through stainless steel tubing from another round bottom flask, a purple-colored solution was formed. This purple Na_2Te solution was transferred into the Cd:2-MPA solution through a stainless steel tubing using argon purge. The reaction flask was dipped into an oil bath of temperature 90°C. The solution turned into orange with time. For Core-shell QDs, 51 mg DMSA was dissolved in 20 ml of distilled water and added into the mixture after 4 h to form the CdS shell around the 2-MPA coated CdTe core through DMSA decomposition. The mixture was stirred until QDs emitting in the desired λ range were obtained.

3.1.2.2 Synthesis of QDs inside Zn-Al-SDS LDHs through Complex Exchange

The $\text{Cd:}(\text{SCH}_2\text{CH}_2\text{COOH})_2$ and $\text{Pb:}(\text{SCH}_2\text{CH}_2\text{COOH})_2$ complexes were prepared by dissolving proper amounts of cadmium (100.4 mg)/lead (126 mg) nitrate and 2-MPA (63 μl) in 150ml of decarbonated water, separately. The pHs of the solutions were adjusted to 7.5 and 11, respectively. The complex solutions were then mixed with 100mg Zn-Al-SDS LDH overnight. One third of the mixtures were separated for further analysis. The rest of the composite solutions were stirred with 13.2 mg Na_2S for 1 h. The same reaction was repeated with Na_2Te to synthesize CdTe-2MPA at 90°C for 3 h. Composites structures were removed by centrifugation and washed with decarbonated water four times.

For the Cd:DMSA complex, 75.8 mg DMSA was dissolved in 20 ml distilled water at 70°C for 4h and mixed with 79.9 mg cadmium nitrate that was dissolved in 130 ml decarbonated water. The pH of the complex solution was adjusted to 10 and mixed with 100 mg SDS-LDH overnight. The composite was recovered as described above.

3.1.3 Synthesis of Zn-Al-PAA LDH and Zn/Mg-Al-(Cd:($\text{HSCH}_2\text{CH}_2\text{COOH}$)₂)

PAA intercalated Zn-Al LDH was prepared by the urea hydrolysis method as described in chapter 2.2.2 with 100 mM sodium salt of the polyacrylic acid. However, the solution was clear after 48 h and precipitate could be obtained after centrifuging at 3900 rpm for 30 min.

Zn-Al layered materials intercalated with 2-MPA/Cd complex were synthesized by using four different methods. The urea hydrolysis method described before was used for the first two synthetic approach which differs only in the order of addition of reagents.

- I. For Zn-Al-Complex 1, 10mM Zn^{2+} and 5 mM Al^{3+} salts with a mole fraction of $\text{Zn}^{2+}/\text{Al}^{3+}=2$ were dissolved in 130 ml distilled water under Ar in a 4-necked round bottom flask fitted with a mechanical stirrer. The ammonia releasing agent- urea was added onto the mixture with a mole fraction of $\text{urea}/\text{Zn}^{2+}=3.5$. The

$\text{Cd}:(\text{HSCH}_2\text{CH}_2\text{COOH})_2$ complex solution was prepared by dissolving 0.375 mmol $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and 0.75 mmol 2-MPA in 20 ml distilled water, purged with Ar for 5 min, then the pH was adjusted to 7.25 with 10 M NaOH and/or 10 M HNO_3 . A turbid solution was observed immediately upon addition of The $\text{Cd}:(\text{HSCH}_2\text{CH}_2\text{COOH})_2$ complex solution onto the mixture. The mixture was heated at 90°C for 24h. A white precipitate was obtained through centrifugation at 3900rpm for 30 min. It was washed with decarbonated water four times and dried under vacuum before analysis.

- II. For Zn-Al-Complex 2, the $\text{Cd}:(\text{HSCH}_2\text{CH}_2\text{COOH})_2$ complex was prepared first in the flask in 150 ml distilled water and the pH was adjusted to 10.74. Then the metal salts and urea were added on to the mixture before heat treatment. Zn-Al-Complex 2 was also repeated with the addition of extra urea of the same amount of 2-MPA after 24 h and with addition of more extra urea that was four times of the amount of the 2-MPA after 72 h, in two separate reactions. For Zn-Al-Complex 3, HMTA was used instead of urea as ammonia releasing agent.
- III. In Zn-Al-Complex 4, the same reaction was tried with NaOH titration rather than homogenous precipitation.

To synthesize Cd/2-MPA intercalated Mg-Al layered materials, the first method used for Complex 1 was repeated by using Mg^{2+} salt instead of zinc. The same material was also prepared by titrating the solution of $\text{Cd}:(\text{HSCH}_2\text{CH}_2\text{COOH})_2$ complex (10 mM $\text{Cd}(\text{NO}_3)_2$ and 20 mM 2-MPA) with a solution of magnesium and aluminum salts (40 mM Mg^{2+} and 20 mM Al^{3+}) together with NaOH until pH reached 9. The mixture was stirred at room temperature for an hour and kept at 90°C for 72 h. A pale yellow powder was obtained after centrifuging at 3900 rpm for 30 min. The powder was washed with distilled water for four times and dried under vacuum.

3.1.4 Synthesis of Mg-Al-CO₃ LDH and Ion Exchange with NO₃²⁻

Mg-Al LDH was synthesized urea hydrolysis method followed by hydrothermal treatment. 0.333 M magnesium salt, 0.167 M aluminum salt and 0.4 M urea was refluxed under Ar for 24h. The as-synthesized material was then aged in oven at 90°C for 72h. 1 g of the obtained CO₃-LDH was dispersed in 1000 ml aqueous solution of 1M NaNO₃ and 2.5mM HNO₃ to interchange the interlayer carbonate anions for 24 h under Ar purge at room temperature. Material was recovered by filtration and subjected to the nitrate treatment again for another 24h. Finally the NO₃-LDH was filtered and washed with 500 ml of decarbonated water and dried under vacuum.

3.1.4.1 Synthesis of QDs inside NO₃-LDH through Anion Exchange

The NO₃⁻ ions in the intergalery of the Mg-Al-LDH were replaced with Cd:ligand complexes and reacted with Na₂S to synthesize QDs inbetween the layers. The exchange reactions were performed by either forming the complexes in the LDH solution or dispersing the NO₃-LDH in the complex solution.

In the first case (*precursor addition onto LDH*), Mg-Al-LDH was dispersed in decarbonated water first. Appropriate amounts of Cd²⁺ and ligand were then added onto LDH and pH of the solution was adjusted to 7.5. The mixture was stirred overnight. The solution was centrifuged at 3900 rpm and washed with decarbonated water 4 times to remove the excess material. Experiments without this precipitation step were also performed. The precipitates were dried with LABCONCO freeze-drier system and redispersed in 50 ml decarbonated water. The proper amount of Na₂S was dissolved in 50 ml distilled water with sonication and added onto the redispersed LDH material under

Argon. After 1 h reaction, composite materials were removed by precipitation and washed with decarbonated water. The final product was dried on a freeze-drier.

In the second method (*LDH addition onto complex*), LDH was added after the pH of the Cd-ligand solution prepared in decarbonated water was adjusted to 7.5 under Argon. Rest of the procedure applied was the same in both methods. 2-MPA or 3-MPA was used as ligands. The Cd^{2+} / LDH weight ratio was varied from 0.4 to 16 and Cd^{2+} / S^{2-} mole ratio from 2.1 to 3.7. Either 0.7 or 0.35 was used as the Cd^{2+} / ligand mole ratio.

3.1.5 Instrument and Characterization

The crystal structure and crystallinity of the samples were analyzed by powder X-ray diffraction (XRD) with HUEBER G670 diffractometer with a germanium monochromator and Cu-K α radiation at 1.54056Å in 2 θ range from 5° to 100° with 0.005° interval. Data were analyzed by using STOE WinXPOW software. A Bruker axis advance powder diffractometer fitted with a Siemens X-ray gun and equipped with Bruker axis Diffrac PLUS software using CuK α radiation was also used in Sabancı University. The sample was rotated (20 rpm) and swept from 2 θ = 5° through to 80° using default parameters of the program. The X-ray generator was set to 40kV at 40 mA. a Rigaku D/MAX-Ultima+/PC X-ray diffraction equipment was used for the analysis of some powders at Boğaziçi University and Rigaku MiniFlexII was used at Koc University for some of the analysis. The FT-IR spectra were recorded on JASCO FT-IR-600PLUS spectrometer using KBr pallets. Metal amounts were determined by using Inductively Coupled Plasma analysis on a SPECTRO GENESIS EOP ICP. Solutions in triplicates were prepared by dissolving the samples in hot aqua regia. The morphology of the powders was examined with a Leo Supra 35VP Field emission scanning electron microscope, Leo 32 and electron dispersive spectrometer software was used for images and analysis. Imaging

was generally done at 2–5 keV accelerating voltage, using the secondary electron imaging technique in Sabancı University. JEOL 7600F was also used to analyze the morphology of the some of the powders. The optical properties of the powders were analyzed by recording absorbance (UV) and photoluminescence (PL) spectra on a Ocean Optics Maya 2000Pro spectrophotometer fitted with the Hamamatsu S10420 detector in the 300–600 nm range and on Horiba Jobin Yvon–Fluoromax 3 spectrofluorometer with optical fiberglass attachments, respectively. PL spectra were recorded between 400–800 nm at 355 nm excitation wavelengths with a 370 nm filter for CdS QDs and between 410–800 nm at 400 nm excitation wavelengths with a 450nm cut-off filter for CdTe and CdTe/CdS QDs. Brus Equation was used for the size calculation. At least three measurements were performed with different dilutions of the aqueous samples of absorbance ≤ 0.1 at excitation wavelength for quantum yield (QY) calculation. Quantum yields were calculated by comparing the integrated emission of the samples with that of Rhodamine B reference (Rhodamine B in water QY= 31 % at 514 nm) as stated before.¹³⁴

3.2 Results and Discussion

To prepare layered double hydroxide / quantum dot hybrid systems two basic approaches were used: one was to use anion exchange reactions of LDH with pre-made QDs and the second one was to synthesize QDs inside LDH galleries with different methods. Since SDS-LDH was already available, first anion exchange reactions were performed starting with this precursor.

3.2.1 Anion Exchange of Zn-Al-SDS with pre-prepared CdS and CdTe/CdS Core/Shell QDs

SDS-LDH is specifically chosen for the exchange reactions, since it provides a larger intergallery than NO_3 -LDH where the reactions can take place easier. For this purpose 2MPA coated CdS, 2MPA coated CdTe and 2MPA-DMSA coated CdTe/CdS core shell QD was exchanged with the SDS intercalated between the galleries of Zn-Al-LDH. Since very broad peaks are observed for nanocrystals in the XRD diagrams, it is not expected to detect the peaks belonging to the QDs but we expect to see shifts in the LDH peaks together with the change in the interlayer distance. When the XRD profiles of the LDH-SDS, and LDH-QDs are compared, it seems as even if there is a shift, it is to higher 2θ values (Figure 3.1). This observation implies similar or smaller size for QDs than SDS and /or incomplete-no intercalation of the QDs. Sizes of the QDs are calculated to be 2.2 nm for CdS, 2.36 nm for CdTe and CdTe/CdS should be larger than its core. They are all larger than SDS (assumed 2.13 as in chapter 2.1) but in comparable sizes. The other possibility is incomplete or no intercalation. Thermal gravimetric analysis was performed to see changes in the organic content upon exchange with the inorganic QDs (Figure 3.2). When the weight losses at 180-220°C are attributed to the organic content (chapter 2.1), it is clear that almost half of the SDS molecules are exchanged.

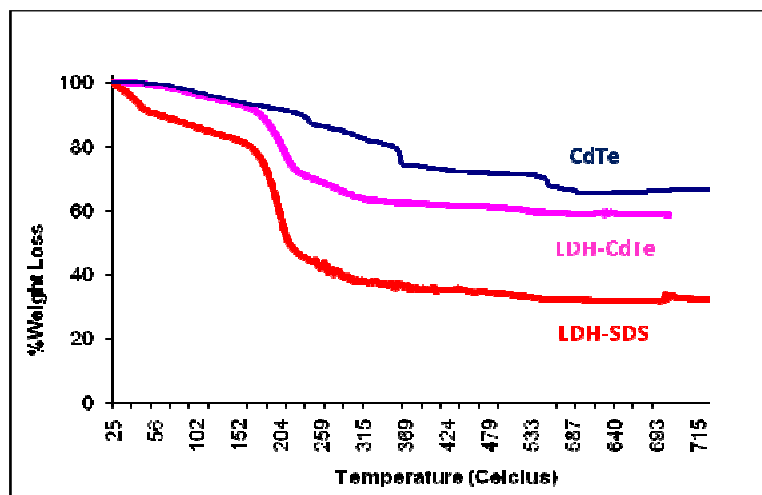


Figure 3.1 Comparison of the weight loss of LDH-SDS, CdTe and LDH-CdTe.

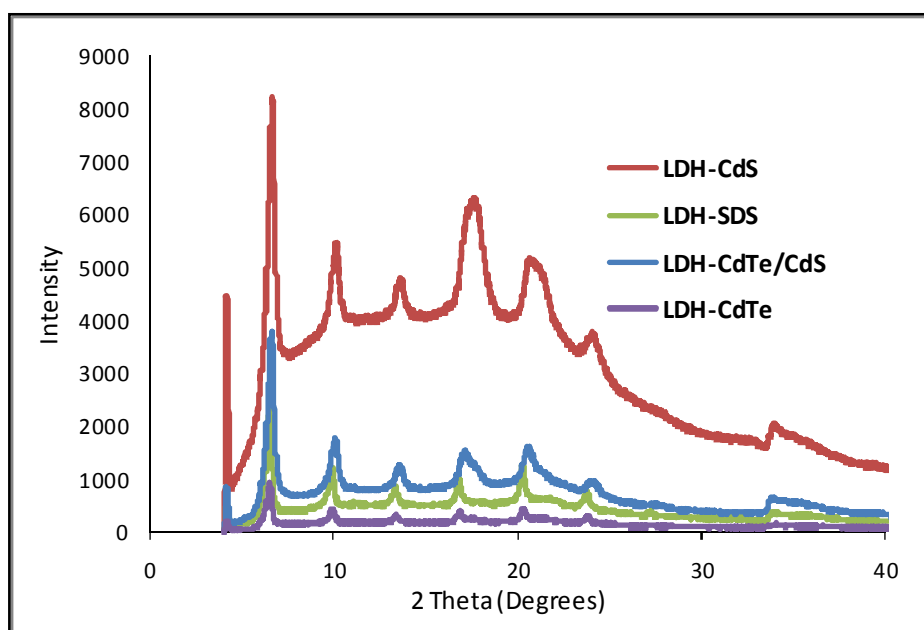


Figure 3.2 XRD Profiles of LDH-SDS and LDH-CdS, LDH CdTe/CdS between 0-40° 2θ range.

In order to see the effect of the encapsulation of the QDs with LDH, the instability tests were performed. The bare QDs and the exchanged QDs were exposed to day-light for prolonged times at room temperature and the photoluminescence spectra were taken at regular intervals. The spectra taken on the 2nd and 16th day of light exposure are presented in Figure 3.3. Intensity loss of the LDH encapsulated QDs are slightly better than the bare QDs in two weeks, being 57.57% and 50.88 %, respectively. The PL max of the bare core/shell QDs increased from 562 to 574 nm when they measured in the powder form which might have occurred due to coagulation of the particles or degradation of DMSA to form a thicker shell when they are dried. This PL max experiences a blue shift to 566 nm after 16 days of irradiation. Degradation in two weeks is consistent with the previous study that specifies 12th day as the beginning of degradation for CdTe/CdS core/shell QDs with DMSA.⁶¹ LDH protects the nanoparticles against this agglomeration or DMSA degradation however, PL max (548 nm) is blue shifted from both aqueous and powder form of bare QDs. For the bare particles, luminescence intensity decreases by almost half and the particle size increases.

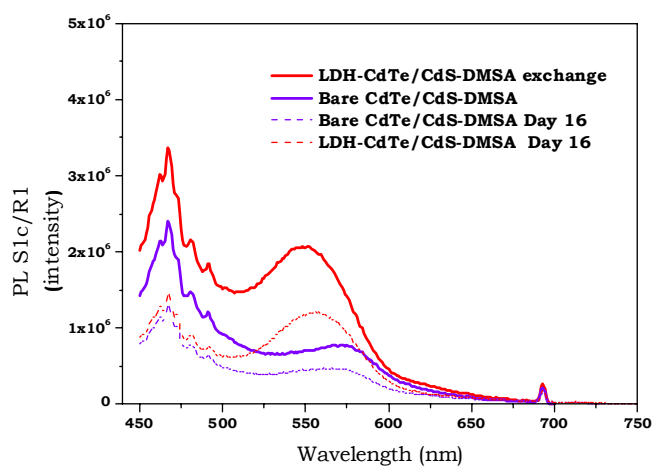


Figure 3.3 Comparison of the stability of the Core/Shell QDs and LDH-Core/Shell.

Venugopal *et al.* argues that the blue shift of the pre-prepared QDs inside the LDH interlayer relies on two factors contributing in different proportions.¹³⁰ The first one occurs due the dilution effect of the QDs in the host matrix. When diluted, less agglomeration is observed for the QDs inside the interlayer hence, delocalization of the energy states is lost. They suggest that since dilution does not always cause the same behavior, the host layer-NP interaction is more dominant to induce the blue shift. As we expected, ‘the strong interaction of the host layer with the NPs eliminates the surface defects and decreases density of the disordered states’.

Another important observation is that the intensity of luminescence is doubled when QDs in LDH are compared with the powder form of bare QDs. This is most probably due to the concentration quenching occurring (reabsorption of the emitted photons) in case of powder QDs and also higher vulnerability to oxidation

3.2.2 Synthesis of QDs inside Zn-Al-SDS LDHs through Complex Exchange

The second approach to obtain the desired hybrid systems was to synthesize the QDs directly in the interlayer. This can be achieved in different ways; the first strategy was the common one used in the literature; exchange of the interlayer anion with complexes that will yield QDs. 2MPA coated CdS, CdTe and PbS as well as DMSA coated CdS was synthesized within the interlayer galleries of Zn-Al-SDS LDHs. For the 2-MPA coated CdS and PbS QDs, firstly the $\text{Cd}:(\text{SCH}_2\text{CH}_2\text{COOH})_2$ and $\text{Pb}:(\text{SCH}_2\text{CH}_2\text{COOH})_2$ complexes were prepared separately and reacted with SDS-LDH after pH adjustment. Then the complex-LDH was dispersed to react with Na_2S or Na_2Te to form the QDs. It was one-pot reaction for DMSA coated CdS since DMSA acts as both stabilizing agent and the

sulfur source on decomposition at high pH and temperature. The reaction parameters are summarized in Table 3.2.

The XRD profiles before and after Na₂S reaction are shown in Figure 3.4. Diffraction profiles do not display a distinct change. Similarly, Lukashin *et al.* didn't observe a significant change after the exchange of NO₃²⁻ anions with thiosulfate complex [Pb(S₂O₃)₂]²⁻, although the peaks are broadened after PbS forms.¹²⁸ For the CdS-DMSA intercalated one, broader peaks are observed for the new LDH. The order in the structure has been lost to some degree. In addition a very small peak appears around 25.87° which might belong to the XRD pattern of CdS QDs.⁶¹ It is not very clear that the other peaks around 30, 42 and 52 are also present or not that belong to the cubic CdS structure, since even they would be very broad and hard to detect under the intense crystalline peaks of LDH. However, only CdTe synthesized in the interlayer exhibit a yellow luminescence upon excitation under 400 nm (Figure 3.5). Yet, failure to observe luminescence might be due to concentration of QDs.

Table 3.2 Synthesis Parameters of QDs inside Zn-Al-SDS LDHs through Complex Exchange

QD Type	SH/Cd (mole:mole)	Cd/S (Cd/Te) (mole:mole)	Cd/LDH (wt:wt)	pH
CdS-2MPA	2.27	3.29	1	7.5
PbS-2-MPA	3.29	3.8	1	11
CdS-DMSA	3.13	0.31	1	10
CdTe-2MPA	2.4	2.6	1	7.5

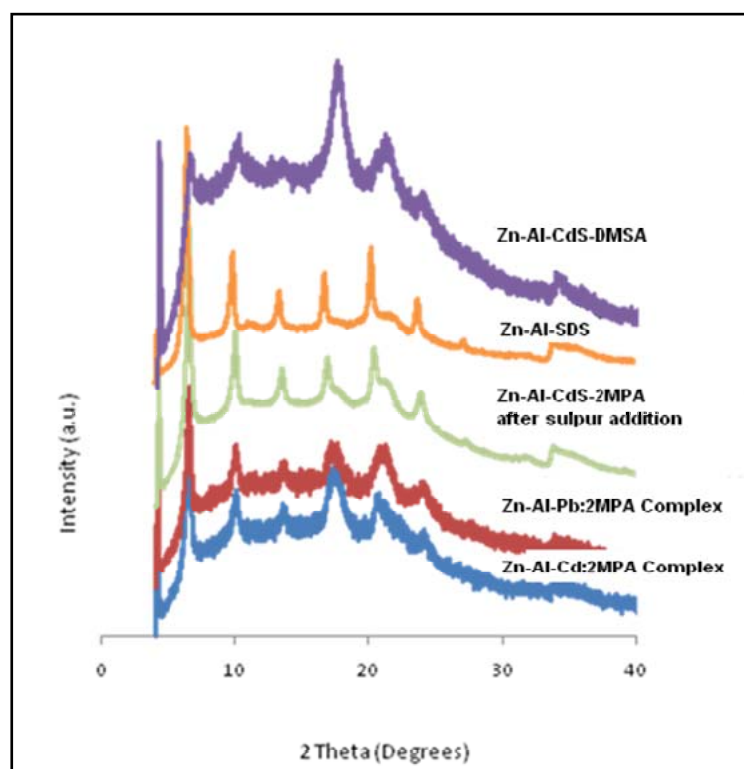


Figure 3.4 XRD Profiles of Cd: Complex Intercalated Zn-Al LDHs and LDH-QDs.

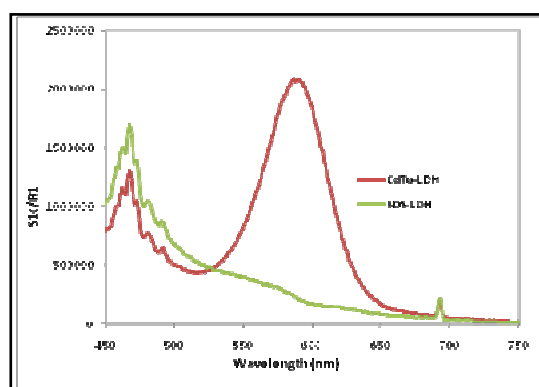


Figure 3.5 PL Spectra of the SDLDH and CdTe-LDH

3.2.3 Synthesis of Zn-Al-PAA LDH and Zn-Al-(Cd:(HSCH₂CH₂COOH)₂)

The second strategy to synthesize QDs directly inside the layers (2nd approach) was to react sulfur/tellurium source with Cd:(HSCH₂CH₂COOH)₂ intercalated LDH or to start from the ligand-intercalated LDH and then add the cadmium and the sulfur or tellurium (Table 3.3). The urea hydrolysis method described in chapter 1-2 was used to prepare LDH. Polyacrylic acid sodium salt was chosen for the ligand-intercalated LDH since it has carboxylate groups that will render the molecule highly anionic and it is known that PAA can stabilize QDs.⁵⁹ LDH-PAA was synthesized under identical conditions with that of LDH-SDS. However, urea amount was not sufficient to increase the pH of the mixture and precipitate formation could not be observed. Even though, NaOH was used to increase the pH from 7 to 10 after 24h of reflux a layered-crystalline structure did not form (Figure 3.6).

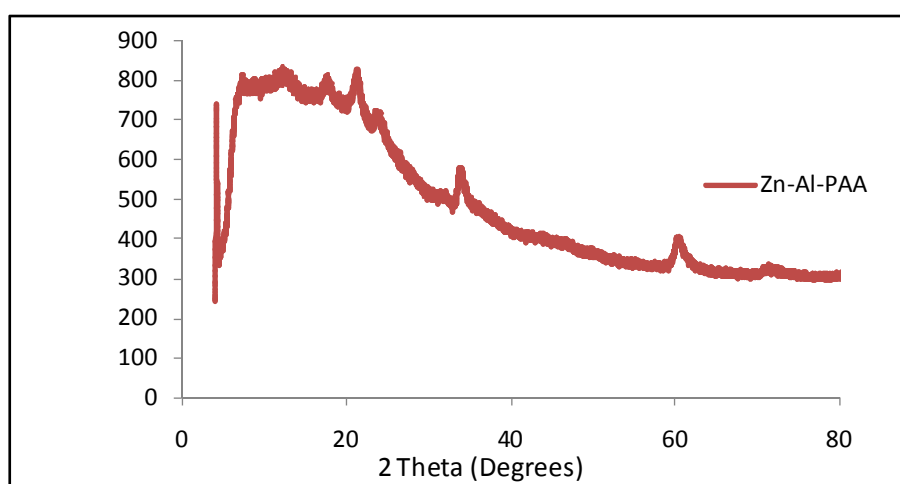


Figure 3.6 XRD Profile of Zn-Al-PAA.

Table 3.3 Reaction parameters for Zn-Al-(Cd:(HSCH₂CH₂COOH)₂) series

Sample	Cd (mM)	2-MPA (mM)	pH Complex	Zn (mM)	Al (mM)	Urea (mM)	pH Reaction End
I	2.5	5	7.5	10	5	35	4.47
II	2.5	5	11	10	5	35	4.5
Ila	2.5	5	11	10	5	40	5.68
Ilb	2.5	5	11	10	5	40+106*	7.30
III	2.5	5	11	10	5	18**	5.70
IV	2.5	5	11	10	5	NaOH Titration	

* Rest of the urea was added as 240 mg after 24 h and 720 mg after 36h.

** HMTA was used instead of urea as ammonia releasing reagent.

Rendering in the pH increase was also observed for Cd:(HSCH₂CH₂COOH)₂ intercalated LDH. For all reactions MPA amount was about equal to the AEC (anion exchange capacity). The complex was prepared at pH 7.5 for Sample I. When the salts are mixed with the intercalated anions, pH immediately drops to 4.2-4.30 and 35mM urea increases the pH to 8.30-8.60 when SDS or SL was used for the intercalation. In case of Cd:(HSCH₂CH₂COOH)₂ complex pH of the mixture stays around 4.5 after 24h of reflux which is not enough for the LDH crystallization. Hence, the complex was prepared at pH 11 for Sample 2. Still, pH decreased after addition of salts and did not increase much till the end of the reaction. After these observations, an extra amount of urea to neutralize the acidity of 2-MPA was used for Sample Ila which did not work either. The same reaction was repeated by using hexamethylenetetramine (HMT) as urea releasing agent. Since HMT generates twice the NH₃ amount released by urea 18 mM HMT was used (Sample III). However, we could increase the pH only to 7.30 after 72h of reflux with 146 mM urea (Sample Ilb). Since the ammonia releasing agents failed to increase the pH to values necessary for the formation of crystalline LDH structures, co-precipitation approach was used as an alternative. LDH formed by the co-precipitation method with NaOH (Sample IV), exhibits sharp X-ray diffraction peaks at 2θ values of 31.84°, 34.48°, 36.26°, 47.84°.

56.78°, 63.1°, 68.29°, and 72.83°. But the main LDH peaks are missing (Figure 3.7). The Mg-Al-Cd:(HSCH₂CH₂COOH)₂ LDH showed similar behavior (Figure 3.8). So, synthesis of LDH with PAA or Cd-ligand complexes has failed.

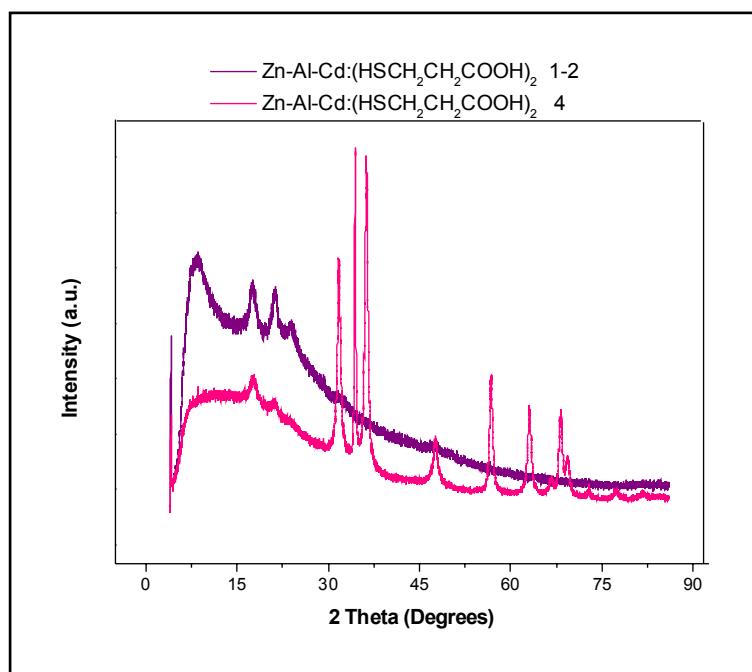


Figure 3.7 XRD Profiles of the Zn-Al- Cd:(HSCH₂CH₂COOH)₂.

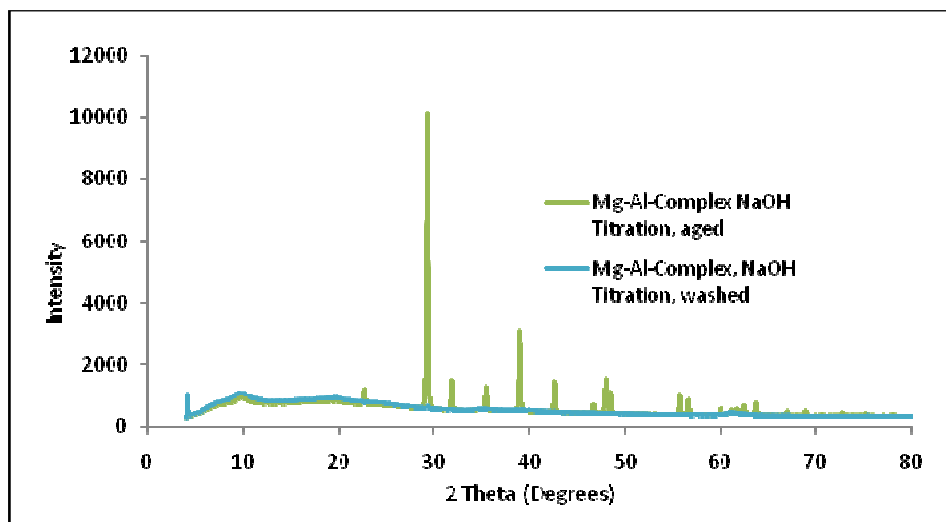


Figure 3.8 XRD Profiles of the Mg-Al-Complex aged for 72 h at 90°C and washed

3.2.4 Synthesis of QDs inside Mg-Al-NO₃-LDH through Anion Exchange

In addition to Zn-Al LDH, Mg-Al LDH was used to construct LDH/QDhybrids, since Mg-Al is generally used in medical applications. Two methods were used to synthesize QDs inside Mg-Al-NO₃ LDH. The first case was *precursor addition onto LDH (PA)* which means cadmium salt and 2-MPA were added at the same time to LDH-NO₃ dispersed in water and then reacted with Na₂S to synthesize CdS QDs in the interlayer galleries of LDHs. The second method was *QD synthesis inside the layers through complex exchange (CE)* as described in the previous sections.

Precursor addition onto LDH

Two series of reactions were performed to analyze the optical properties of QDs. In all sets of reactions bare QDs without LDH were also synthesized under identical condition

to understand if LDH galleries exert any constraints in the crystal growth and/or cause any changes in the quality of the nanoparticles formed. Nitrate intercalated LDHs were used in these reactions. In order to eliminate or minimize QD formation in the solution in addition to the LDH galleries, the precursor intercalated LDHs were precipitated and washed before Na_2S addition. The reaction conditions are summarized in Table 3.4 and 3.6.

Table 3.4 Reaction Conditions for Set I (CdS-2MPA)

Sample	Method	Ppt step	Cd/SH (mole:mole)	Cd/S (mole:mole)	Cd/LDH (weight:weight)
IA	PA	-	0.48	2.5	0.8
IB	-	-	0.48	2.5	No LDH
IC	PA	+	0.48	2.5	0.8

Mg-Al-NO_3 was obtained from the anion exchange of CO_3 intercalated LDH. The completion of the reaction was verified with the XRD diffraction patterns (Figure 3.9). The classical XRD peaks of CO_3 -LDH at 2θ values of 11.38° and 23.33° ¹⁰⁷ are shifted to 9.7° and 19.78° which are characteristic of NO_3 intercalated LDH.⁹⁶ The diffraction profile of IA suggest loss of crystallinity to some degree and new peaks aroused 2θ values around 16° 18° 23° 34° and 52° . However, as stated in the previous sections it is not very clear that the other peaks belong to CdS structure, since even they would be very broad and hard to detect under the intense crystalline peaks of LDH (valid for IIA, Figure 3.13).

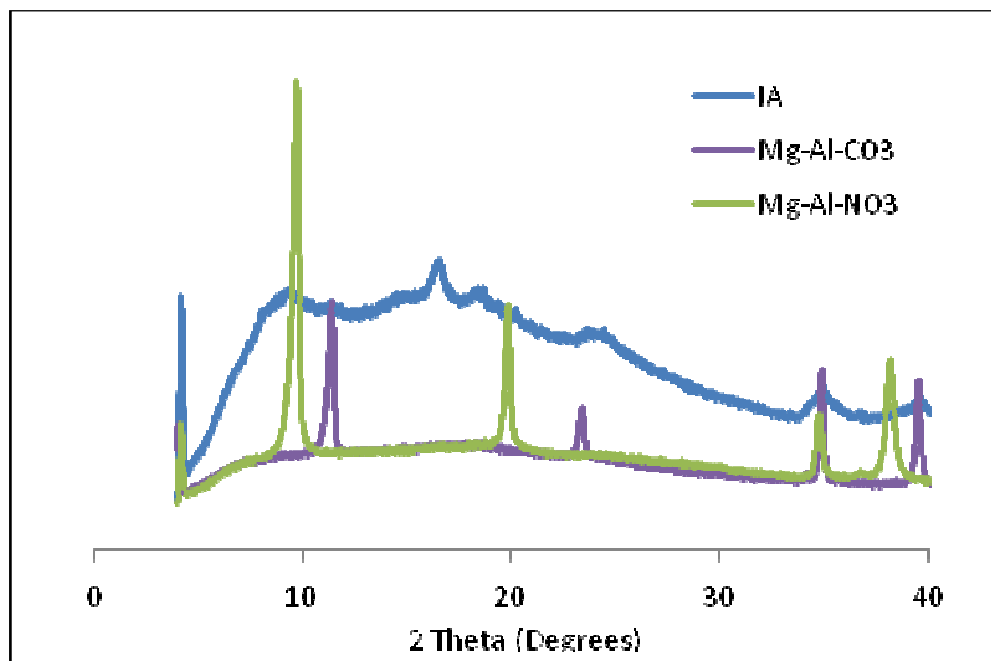


Figure 3.9 XRD Profiles of MgAl-CO₃ Mg-Al-NO₃ and Mg-Al-CdS-2MPA (IA)

Luminescent LDH was obtained by synthesizing QDs inside LDH layers (IA, IC). The luminescence behavior of IA and IB are shown in Figure 3.10. Bare QDs (IB) are shown to be superior to LDH/QD material synthesized under the same conditions with a QY of 53% (Table 3.5). One of the most significant observation was nanocrystals were formed both inside and outside of the layers since the supernatant of IA is also luminescent. This is not unexpected since the Cd/2MPA complex that was not intercalated was not washed off before sulfide addition in this reaction (Figure 3.10). Secondly, the PL maximums of the LDH/QD hybrids are red shifted by 95-109 nm suggesting smaller size for bare QDs as opposed to the literature¹³⁰ and the results obtained for the QDs synthesized inside Zn-Al LDH through complex exchange (Section 3.3). This size

difference might stem from the fact that some of the MPA has exchanged the NO_3 anions in the intergallery and therefore ligand amount available for CdS stabilization has decreased. But the same amount of Na_2S used in all reactions; hence Cd/S ratio inside the galleries might be possibly lower. This argument is consistent with the observation of PL max increase of 98 nm with decreased Cd/S ratio before with CdS-2MPA by Acar *et al.*⁶⁰ In addition, the precipitate of IA did not show any luminescence which offers bulk CdS formation since Cd incorporation is verified with ICP-AES. Bulk CdS formation is also consistent with the absorption onset of around 520 nm¹³⁵ (Figure 3.11) which supports further the lower Cd/S ratio inside the layers. IC was not luminescent either as IA precipitate this fact implies that only free QDs formed.

Table 3.5 Optical Properties of Series I (CdS-2MPA).

Sample	Peak Maximum	Quantum Yield %
IA stock	585	6.30
IA supernatant	599	0.57
IB CdS-2-MPA	490	53.57

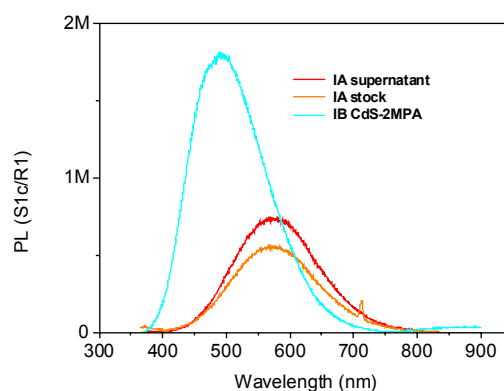
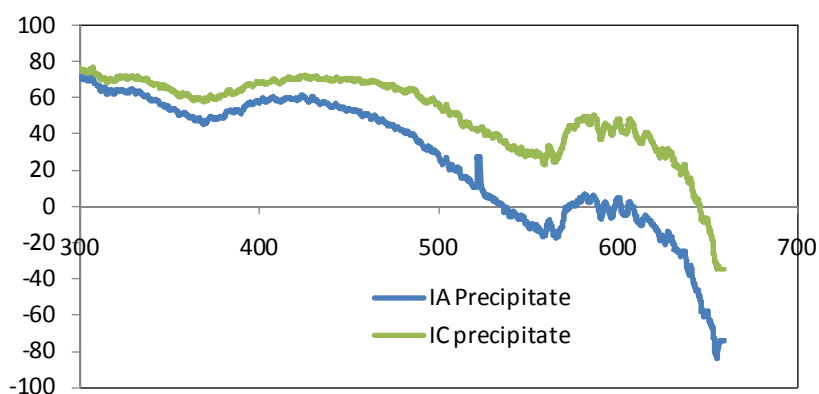


Figure 3.10 PL Spectra of Series I (CdS-2MPA).

Table 3.6 Reaction Conditions for Set II (CdS-2MPA)

Sample	Method	Ppt step	Cd/SH (mole:mole)	Cd/S (mole:mole)	Cd/LDH (weight:weight)
IIA	PA	+	0.7	2.5	0.8
IIB	-	-	0.7	2.5	No LDH

**Figure 3.11** Absorbance spectra of IA and IC : LDH/CdS-2MPA.

In the second series Cd/SH ratio is lowered to tune the color of luminescence of the QDs (Table 3.6). Nanocrystals were obtained from the precipitate of the LDH/QDhybrid (IIA) with a nice peak on PL spectra (Figure 3.12). The blue shift of 60 nm from around 585 (IA stock) to 525 nm (IIA) of PL max is consistent with the observation of blue shift with increasing Cd/SH ratio.⁶⁰ It seems there is a red shift in PL max of the bare QD (490 nm for IB and 507 nm for IIB) however; dried sample was used for the analysis in the second case to be more accurate in comparison whereas the calculations were performed with the aqueous solution in the first case. The drying process might have caused

agglomeration as discussed in the previous sections. As seen in the first series, bare QDs seem to be composed of smaller crystals than the ones constructed inside the layers.

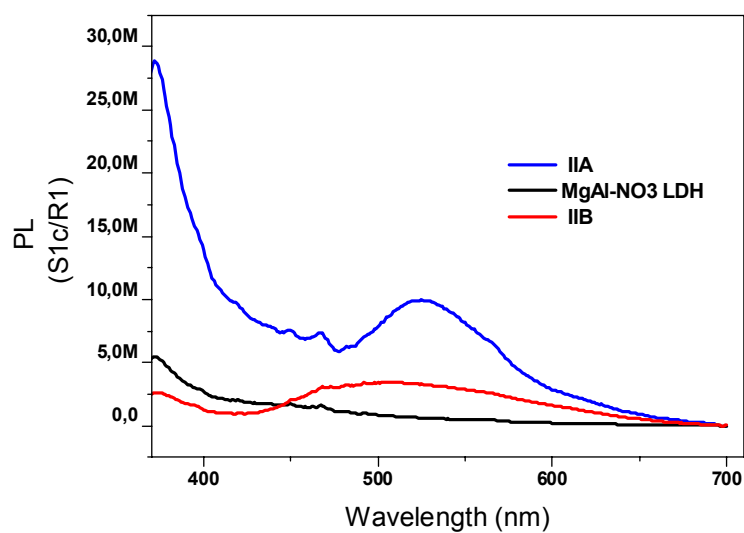


Figure 3.12 PL Spectra of Series II

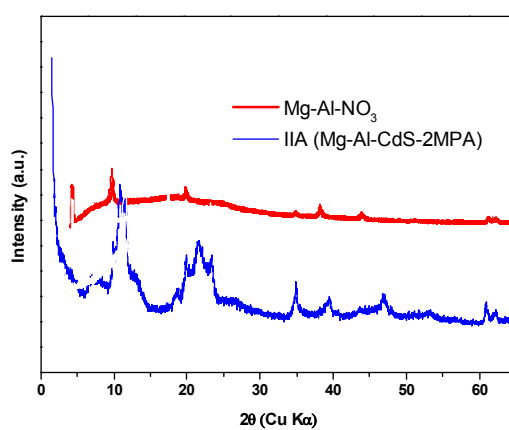


Figure 3.13 XRD Profiles of IIA and Mg-Al-NO

CdS-3MPA inside LDHs through Complex Exchange

Even though the QY of 3MPA stabilized QDs are significantly lower than CdS-2MPA⁶⁰, to optimize the reaction parameters 3MPA coated QDs are chosen. Since the thiol group of the 2MPA is more hindered compared of the thiol of 3MPA, the intercalation might be easier for complex exchange reactions with 3MPA. The Cd/LDH ratio was increased 8-fold to ensure sufficient amount of complex intercalation to synthesize QDs. The Cd/S ratio was also increased to 21.5 to ensure smaller size for the nanocrystals. In addition two methods *precursor addition onto LDH (PA)* and *QD synthesis inside the layers through complex exchange (CE)* are compared. (The reaction parameters are summarized in Table 3.7).

Table 3.7 Summary of the Series II and IV (Luminescent QDs (yellow)).

Sample	Method	pH	PL Max (nm)	PL Max* (nm)	Cd/LDH (weight/weight)	Cd/S (mole/mole)	Cd/SH (mole/mole)	Temp (°C)	Time (h)
IIA	PA	7.40	525	507	0.8	2.1	0.7	RT	1
IIIA	PA	7.2	—	—	6.5	21.5	0.53	RT	1
IIIB	CE	7.2	—	—	6.5	21.5	0.53	RT	1
IIIC	CE	9.2	—	—	6.5	21.5	0.53	RT	1
IVA	CE	7.40	554	548	8.0	2.5	0.7	RT	1
IVB	CE	7.50	541	553	8.0	3.7	0.7	RT	1
IVC	CE	7.50	540	565	16.0	2.6	0.7	RT	1
IVD	CE	7.50	537	563	8.0	2.5	0.7	90°C	0.5
IVD	CE	7.50	542	563	8.0	2.5	0.7	90°C	1
IVD	CE	7.50	544	564	8.0	2.5	0.7	90°C	3
IVD	CE	7.50	540	567	8.0	2.5	0.7	90°C	18

* PL Max of the bare QD synthesized under identical conditions

In the third reaction series Cd/S ratio was increased almost 10-fold since the size difference of the QDs synthesized inside and outside the layers was attributed to excess sulfur. However, the effect of decreased sulfur amount could not be observed since luminescent hybrid was not obtained with either of the methods for reaction series III. reaction pH was 7.2 (IIIB) which was reported to be the optimum pH that yields best QY for CdS-3MPA.⁶⁰ The reaction pH was increased to 9.2 (IIIC) which would render the complex more anionic through ionization of the carboxyls to enhance the intercalation amount of the complex. Increased pH did not yield luminescent hybrid either. However, the cadmium and sulfur content in the LDH structure was confirmed with ICP analysis. Luminescent hybrids were obtained when Cd/SH ratio was increased to 0.7 and Cd/S ratio decreased to the value before with the complex exchange method (IIA). The reaction temperature was increased to 90°C, to increase the particle size and luminescent LDH array in different emission colors. Temperature did not affect the size of the particles formed either inside or outside the LDH galleries. In all cases, QDs formed inside are smaller than the bare QDs. Some of the ligand is probably used for the NO₃ exchange decreasing the ligand/Cd ratio which results in the formation of larger QDs.

The morphology of the Mg-Al LDH does not change after the hybrid formation (Figure 3.14). In addition, the small particulates in addition to plates observed in Figure 3.15 are indication of the formation of CdS since EDX patterns show the presence of Cd and S on these particles. When the XRD profiles of the precursor LDH and the hybrid before and after Na₂S addition was compared, along with a shift in the position of the main peak extra peaks that can be attributed to CdS appear which might be related to the surface bound QDs rather than intercalated CdS (Figure 3.15). Whatever the locations of the nanoparticles are, luminescent LDH was obtained that can be used for labeling, tracing and delivery of biological materials.

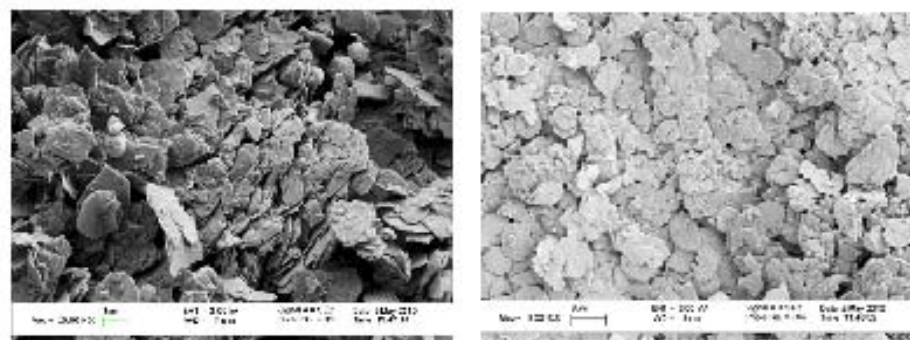


Figure 3.14 SEM photographs of the Mg-Al- CO_3 LDH (Left) and Mg-Al-CdS- 3MPA (Right)

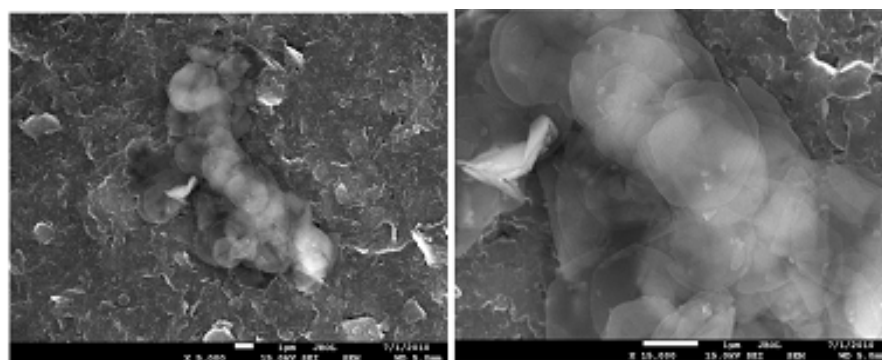


Figure 3.15 SEM images of IVB at different magnifications

In order to determine the effect of the encapsulation of QDs with LDH, stability of both bare QDs and LDH/QDs were tested. Both were exposed to day-light for prolonged times at room temperature and the photoluminescence spectra were taken at regular intervals. The spectra taken on day 9, 13 and 24 of light exposure are presented in Figure 3.17. Intensity losses of the bare and encapsulated QDs are similar in four weeks. Both spectra show a decrease in the intensity for the first 9 days 88% for LDH/QD and 49% for

bare QD and then an increase. The intensity of LDH/QD is increased by 17% from day 9 after 24 days and that of bare QD decreased by 29% from day 9 on day 24. PL max of LDH/QD decreases from 558 nm to 520 nm and increases to 562 nm, again. PL max of bare QD did not show a significant change in the first 9 days but increased from 547 nm to 567 nm in 24 days. Size decrease in two weeks stem from the degradation of the organic ligand at room temperature and oxidation of the surface in daylight. The red shift of PL max might be attributed to the coalescence of the particles in prolonged light exposure. Actually, if an oxide is formed around CdS after the initial loss of the coating ligand, a blue shift is expected. An oxide layer can act as a larger band gap coating causing a slight increase in the luminescence.

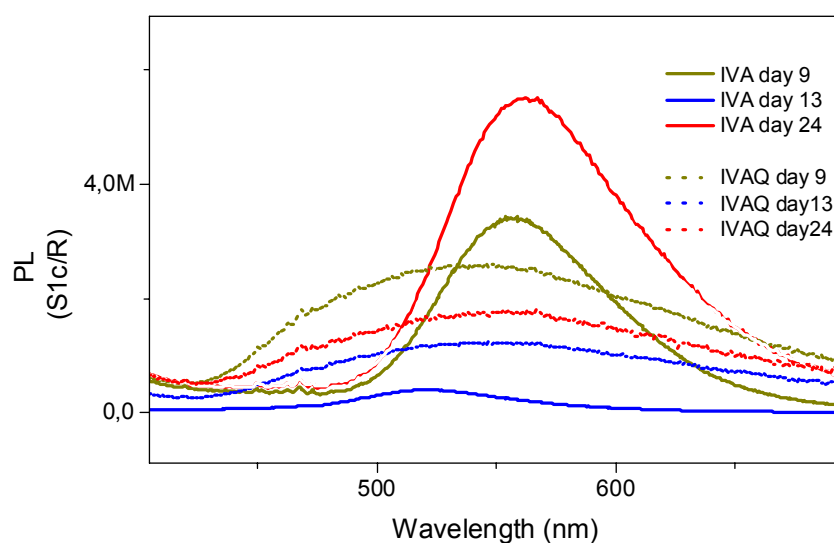


Figure 3.16 Photoluminescence stability of bare (IVAQ) QDs and LDH/QDhybrid (IVA) synthesized under identical conditions

3.3 Conclusions and Prospects

Luminescent LDH/QD hybrids were obtained successfully both by anion exchange of pre prepared QDs and direct synthesis of the QDs inside the galleries. As expected, the anion-exchange was a simpler method whereas different methodologies have to be applied to form the hybrids with direct synthesis.

In the anion-exchange method, 50% of SDS could be exchanged with pre-prepared QDs. QDs in the hybrid shows a blue shift as compared to the bare QDs in the powder form depending on the interaction of the QDs with the host material. Increase in the intensity of luminescence was observed for LDH/QD which is attributed to concentration effect. When bare QDs are dried they experience concentration quenching whereas the QDs in the hybrids are diluted.

To directly synthesize QDs inside the layers three different strategies were used. One of the approaches was to synthesize ligand intercalated LDH and then react that material with Cd and S (or Te) which did not work. Ligand intercalated LDH in a well crystallized form could not be obtained since pH of the reactions did not reach the desired value. The second strategy was to exchange the NO_3^- anions in the intergallery with ligand and Cd by adding each one into the dispersed LDH solution. When Cd/SH ratio was 0.48 free QDs formed in the presence of LDH which are larger than the bare QDs synthesized under identical conditions and bulk CdS obtained inside the layer. To ensure larger QD formation Cd/SH ratio was increased to 0.7. In this case, luminescent hybrids could be obtained which are smaller than bare QDs due to smaller Cd/S ratio inside the layers. The last strategy was to exchange pre-formed Cd:ligand complexes at a certain pH with SDS/ NO_3^- anions. This method was not successful for 2MPA due to the hindered SH- group and DMSA. Lumisencent LDH/QD hybrids were obtained with 3MPA for Cd/SH=0.7, Cd/S=2.5 (and 3.7) and Cd/LDH=0.4, 0.8, 16. The sizes of the QDs in the hybrids are

smaller than the bare QDs which can be attributed to different ligand/Cd and Cd/S ratio. Another possibility is the physical limitation enforced by the LDH sheets. QDs emitting in different colors than yellow could not be obtained in the hybrid structures.

Precursor addition or complex exchange can be further used to synthesize CdTe-3MPA, CdSe-3MPA QDs or CdTe/CdS, CdTe/CdSe⁷⁴ and CdSe/ZnTe core/shell structures.⁷⁴

Chapter 4

CONCLUSIONS

This thesis work was devoted to develop hybrid layered double hydroxide nanoparticles. Firstly, organic/inorganic hybrids were constructed by intercalating surfactants to Zn-Al LDHs as described in chapter 2. These hybrids as well as Mg-Al-NO₃ LDH were used to form LDH/QD hybrids which was summarized in chapter 3.

In the first part, the effect of surfactants with different head groups on the morphology of layered double hydroxides was explored. LDH intercalated with SDS revealed different morphologies with varying concentration of SDS. SDS concentration lower than CMC yielded coral-like LDHs when the concentration was one to three times of the anion exchange capacity (AEC) reported in literature. However, when SDS concentration was dramatically higher than CMC and AEC (20-fold), hollow rings of stacked LDHs were observed for the first time. Two factors are believed to be contributing in the formation of this morphology; the shape of the surfactant micelles in 100 mM SDS, 5 mM aluminum salt, 10 mM zinc salt and 35 mM urea at 90°C and templating effect of the excess surfactant. However, when a surfactant of similar size with –COOH end group was used, not only the morphology but also the chemical composition was changed. Rod-like layered zinc hydroxide intercalated with SL was obtained when sodium laurate was used under the identical reaction conditions which were also new in the literature. Interestingly, the aspect ratio of the rods was dependent on the Zn/Al ratio. These surprising results are believed to stem from the preferential interactions of surfactants with the metals. Determination of exact CMC and the

surfactant shape under these synthesis conditions as well as the stability and solubility of the metal-ligand complexes should be analyzed further to understand the formation of these systems.

In the second part, the as-synthesized SDS-LDH was used to construct LDH/QD hybrids either by exchanging SDS with pre-prepared QDs or Cd:ligand complexes. The luminescence of the exchanged QDs (CdS-2MPA, CdTe-2MPA, 2MPA-DMSA coated CdTe/CdS) were blue-shifted which was attributed to the dilution effect and the special interaction between the host and the QDs. The LDH/QD hybrids prepared through the exchange of Cd:2MPA complex with SDS were not luminescent. Major problem in such an approach may be the lack of control in ligand/Cd ratio. In addition, the attempt to prepare PAA and Cd:2MPA intercalated LDH and to synthesize QDs in the intergaller of LDH by adding cadmium (for PAA) and sulfur source was unsuccessful since urea hydrolysis did not increase the pH more than around 7.

Since the aim of this study was to improve the potential of LDHs as biological carrier molecules with QD incorporation which will allow the hybrid to be tracked, nontoxic, biocompatible Mg-Al-NO₃ LDH was chosen for the optimization of the hybrid preparation with Cd:ligand exchange. 3MPA was used for the following procedures instead of 2MPA since it did not contain sterically hindered -SH group. Luminescent, smaller QDs in the hybrids than the QDs synthesized without LDH under identical conditions were obtained with Cd/S=2.5 (and 3.7), Cd/SH=0.7, Cd/LDH=0.4, 0.8, and 16 due to different SH/Cd as well as ligand/Cd ratio within the layers. Increasing the reaction temperature for prolonged times did not yield larger particles that emit in significantly longer wavelengths. LDH may be exerting a physical limit to crystal growth. When the ligand and Cd were added on aqueous solution of LDH at the same time and reacted with Na₂S, QDs were formed only in solution outside of the interlayer galleries and they were larger than bare QDs (Cd/SH=0.48, Cd/S=2.5, Cd/LDH=1). Exchange of the existing anions with the ligand decreases the ligand/Cd ratio causing larger particles. Bulk CdS formed inside the layers. Smaller QDs in the

hybrid than QDs in solution with this method were obtained when Cd/SH ratio was increased to 0.7 and when the mixture was precipitated and washed before Na₂S addition. As a summary, we have shown that under identical conditions preparation of QD in the interlayer gallery versus in solution results in particles with different size and quality. Overall, it is clear from the results that when QDs are formed in the interlayer galleries, it is difficult to control size and concentration since the ligand used to coat the QD surface and hence control crystal growth and quality, partly used to exchange the anions (NO₃ or SDS) residing in the interlayer galleries. In addition, the Cd/S ratio is difficult to control. Besides LDH layers may exert a physical limit for growth. Yet, hybrids can be formed by exchanging the anions with pre-made QDs. In such hybrids good luminescence can be achieved.

Preliminary stability studies show that being encapsulated within the layers does not improve the optical properties and stability of the QDs. This study can be extended to form CdSe, CdTe, CdTe/CdS, CdTe/CdSe and similar structures to analyze the change in the optical properties deeper. The cell-viability tests and imaging experiments will be performed in the near future.

APPENDIX

CALCULATION OF QUANTUM DOT SIZE BY BRUS EQUATION FROM ABSORBANCE SPECTRUM

Particles size of QDs is estimated from their absorption edges as proposed by Brus⁶² in 1984 as shown in Eqn. A.1.

$$E_g(dot) = E_g(bulk) + E_k + E_{Coul} \quad (A.1)$$

where, E_g represents bulk band gap energy of the semiconductor,

E_k is quantum well approximation and

E_{Coul} is Coulomb interaction.

E_g , E_k and E_{Coul} should be calculated and inserted in Eqn. (A.1) to estimate the particle size.

$$h \frac{c}{\lambda_{edge}} = E_g(bulk) + \frac{h^2}{8r^2} \left[\frac{1}{m_e^*} + \frac{1}{m_h^*} \right] - 1.8 \frac{e^2}{4\pi\epsilon\epsilon_0 r}$$

(A.5)

$$E_k = \frac{h^2}{8r^2} \left[\frac{1}{m_e^*} + \frac{1}{m_h^*} \right]$$

(A.3)

$$E_{Coul} = -1.8 \frac{e^2}{4\pi\epsilon\epsilon_0 r}$$

(A.4)

Bulk band gap energy of the semiconductor (E_g);

$$E_g(dot) = h\nu_{edge} = h \frac{c}{\lambda_{edge}} \quad (\text{Eqn. A.2})$$

Substituting $c = 3.0 \times 10^8 \text{ m/s}$, E_g , can be found as;

$$E_g(dot) = h \frac{c}{\lambda_{edge}} = 4.13566 \times 10^{-15} [eV \cdot s] \frac{3.0 \times 10^8 \left[\frac{m}{s} \right] \times 10^9 \left[\frac{nm}{m} \right]}{\lambda_{edge} [nm]} \quad (\text{Eqn. A.3})$$

$$E_g(dot) = \frac{1240.7 [eV \cdot nm]}{\lambda_{edge} [nm]}$$

The λ_{edge} (absorption edge) is the point of intersection of the line passing through the reference region and the line drawn at the linear region of the absorbance (illustrated in Figure A.1.) in the absorbance spectrum.

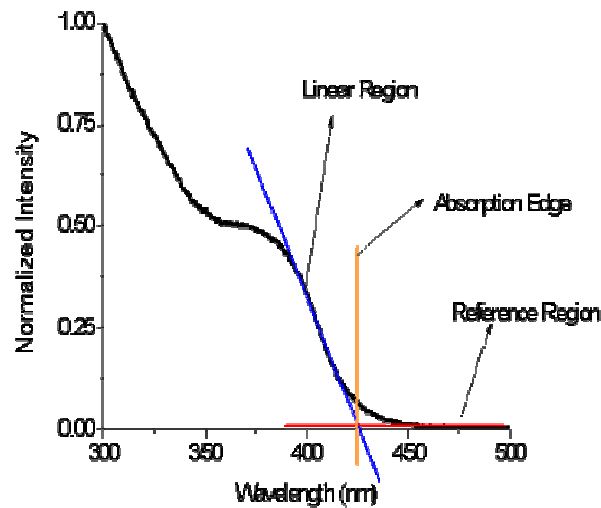


Figure A.1 Representative plot of the absorption edge determination

Quantum well approximation (E_k);

Substituting the constants,

$$m_e = 9.10938188 \times 10^{-31} \text{ kg}$$

$$h = 6.62606 \times 10^{-34} \text{ Js} = 4.13566 \times 10^{-15} \text{ eVs}$$

E_k is calculated as;

$$E_k = \frac{h^2}{8r^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) = \frac{(4.13566 \times 10^{-15} [\text{eV} \cdot \text{s}])^2}{8 \times (r[\text{nm}])^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right)$$

$$E_k = \frac{2.13796 \times 10^{-30} [\text{eV} \cdot \text{s}]^2}{(r[\text{nm}])^2} \left(\frac{1}{m_e^* [\text{kg}]} + \frac{1}{m_h^* [\text{kg}]} \right) \times \frac{[\text{kg} \cdot \text{m}^2 / \text{s}^2]}{[\text{J}]} \times \frac{1.602 \times 10^{-19} [\text{J}]}{[\text{eV}]} \times \frac{(10^9 [\text{nm}])^2}{[\text{m}]^2}$$

$$\boxed{E_k = \frac{3.425 \times 10^{-31} [\text{eV} \cdot \text{nm}^2]}{(r[\text{nm}])^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right)} \quad (\text{Eqn. A.4})$$

Coulomb interaction energy (E_{Coul});

Substituting the constants,

$$e = 1.602 \times 10^{-19} \text{ C}$$

$$\epsilon_0 = 8.854 \times 10^{-12} \frac{\text{F}}{\text{m}} \text{ or } \frac{\text{C}}{\text{Vm}}$$

E_{Coul} is calculated as;

$$E_{\text{Coul}} = -1.8 \frac{e^2}{4\pi\epsilon_0 r} = -1.8 \frac{(1.602 \times 10^{-19} [\text{C}])^2}{4 \times \pi \times \epsilon \times 8.854 \times 10^{-12} \left[\frac{\text{C}}{\text{V} \cdot \text{m}} \right] \times r[\text{nm}]} \times \frac{[\text{eV}]}{1.602 \times 10^{-19} [\text{CV}]} \times \frac{10^9 [\text{nm}]}{[\text{m}]}$$

$$E_{Coul} = -\frac{2.592[eV.nm]}{\varepsilon \times r[nm]} \quad (\text{Eqn. A.5})$$

Inserting $E_g(\text{dot})$ (A.11), $E_g(\text{bulk})$, E_k and E_{Coul} terms into Eqn. (A.1), the following equation is obtained;

$$\frac{1240.7[eV.nm]}{\lambda_{edge}[nm]} = E_g(bulk) + \frac{3.425 \times 10^{-31}[eV.nm^2]}{r[nm]^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - \frac{2.592[eV.nm]}{\varepsilon \times r[nm]}$$

Since $d = 2 \times r$;

$$\frac{1240.7[eV.nm]}{\lambda_{edge}[nm]} = E_g(bulk) + \frac{1.37 \times 10^{-30}[eV.nm^2]}{(d[nm])^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - \frac{5.184[eV.nm]}{\varepsilon \times d[nm]} \quad (\text{Eqn. A.6})$$

A.1 CdS Particle Size Calculation

To calculate the size of the CdS QDs the following parameters should be inserted into Equation A.6;

$$\begin{aligned} m_e^* &= 0.3m_e \quad \text{where} \quad m_e = 9.10938188 \times 10^{-31}[kg] \\ m_h^* &= 0.8m_e \end{aligned}$$

$$E_{g,CdS} = 2.58eV$$

$$\varepsilon = 5.7$$

And finally the following equation is obtained for CdS;

$$\frac{1240.7[eV.nm]}{\lambda_{edge}[nm]} = 2.42[eV] + \frac{6.893[eV.nm^2]}{(d[nm])^2} - \frac{0.909[eV.nm]}{d[nm]} \quad (\text{Eqn. A.7})$$

A.2 CdTe Particle Size Calculation

To calculate the size of the CdS QDs the following parameters should be inserted into Equation A.6

$$\begin{aligned} m_e^* &= 0.14m_e \\ m_h^* &= 0.37m_e \end{aligned} \text{ where } m_e = 9.10938188 \times 10^{-31} [kg]$$

$$E_g, CdTe = 1.50 eV$$

$$\varepsilon = 10.6$$

And finally the following equation is obtained for CdTe

$$\boxed{\frac{1240.7 [eV \cdot nm]}{\lambda_{edge} [nm]} = 1.50 [eV] + \frac{14.8 [eV \cdot nm^2]}{(d [nm])^2} - \frac{0.489 [eV \cdot nm]}{d [nm]}} \quad (\text{Eqn. A.8})$$

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