Layered Double Hydroxides: Tailoring Interlamellar Nanospace for a Vast Field of Applications

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Abstract

Fifty-eight years ago, in his famous lecture at the California Institute of Technology, Richard Feynman stated: “What I want to talk about, is the problem of modifying and governing the world of the infinitely small. I said: ‘What I have demonstrated is that there is room—that you can decrease the size of things in a practical way. I want to show that there is plenty of room. I will not now discuss how we are going to do it, but only what is possible in principle… We are not doing it simply because we haven’t yet gotten around to it.’ Useless to say how profound his sensibility for science was. We’ve just begun to walk in this enormous field, toward the assembly of devices atom by atom. What we did till now is still rudimentary. Anyhow we believe that Layered Double Hydroxides could play a role in manufacturing these nanometric equipments.

Layered Double Hydroxides (LDHs) are 2D ionic lamellar nano-materials belonging to the group of anionic clays. Their structure consists of positively charged brucite-like layers and intercalated anions. The layered structure, together with the flexibility to intercept different anionic species in variable compositions, both inorganic and organic, has attracted increasing interest. In order to meet specific requirements in very distant fields, considerable efforts were made to tailor the physical/chemical properties of LDHs and design engineered LDHs for several applications, ranging from anticorrosion coatings, flame-retardants, catalysis, to water treatment/purification, and biomedical applications. Furthermore they have been applied in energy harvesting and conversion, thanks to the possibility of substituting the composing metals with transition metals.

Within the framework of this contribution, we first briefly review the development of synthesis processes (§1). In Paragraph 2, examples of the LDHs applications are reported. We will then focus on our laboratory experimental activities, showing the growth of the structures either on printed circuit tracks for applications of LDHs as gas sensors and biosensors. One more application is in nanostructured-modified textiles.

Introduction

Layered Double Hydroxides (LDHs) are 2D ionic lamellar materials belonging to the group of anionic clays. The structure of LDHs is based on brucite-like layers containing both divalent M$^{2+}$ and trivalent M$^{3+}$ cations coordinated to six OH$^{-}$ hydroxyl groups [1,2]. It can be expressed by the formula $[[\text{M}^{2+}_{x-1}\text{M}^{3+}_x\text{OH}_2]_n\text{A}^+(\text{An})_x]/m\text{H}_2\text{O}$. The substitution of the divalent M$^{2+}$ metal cation with a trivalent M$^{3+}$ one, due to the charge disequilibrium, gives rise to the infinite repetition of positively charged sheets (lamellas) alternating with An$^+$ ions (Figure 1) which are required to balance the net positive charges of the hydroxide layers. The molar ratio $x$=M$^{2+}$(M$^{3+}$+M$^{2+}$) generally ranges within the interval (0.2-0.4).

The layered structure has attracted increasing interest since it makes LDHs the ideal system for pursuing material engineering at a nanometric scale by using chemical methods. Experimental results obtained so far have shown that this statement is mainly based on three reasons. First, researchers have a large variety of choice for the two cation metals, with a consequent wide range of structural, physical and chemical properties; second, the repetition of interlamellar domains enables designing a solids with an accessible internal surface up to 800 m$^2$/g. Third, and most importantly, LDHs can host and exchange mixed valence metal ions, water molecules and even relatively complex organic molecules, intercalated in the inter-lamellar space. These almost unique physical/chemical properties have been exploited to shape LDHs and meet specific requirements for LDHs in very distant fields. In fact, engineered LDHs can find a huge variety of applications.

Keywords: Nano-materials; Biosensors; Anticorrosion coatings; Morphology

For instance, by intercalation with appropriate anionic molecules, they have been investigated as additives in super hydrophobic surfaces [1], anticorrosion coatings [2,3], flame-retardants [4], catalysis [5], water treatment and purification [5,6], biomedical applications (e.g. drug delivery and biosensors) [7,8], and in many other fields. Furthermore, by using transition metals as the component cations, they have been suggested as promising materials in energy harvesting and conversion [9].

Within the framework of this contribution, we first briefly review structures and compositions (§1), the development of synthesis processes (§2). In Paragraph 3, examples of the most recent applications of LDHs are reported. We will then focus on our experimental activities, reporting on the growth of LDH nanostructures on different substrates, either for biosensor or for physical/chemical microsensors. Results of different characterization techniques will also be reported. Section 4 will be addressed to the possible related applications of LDHs as gas sensors, biosensors, and nanostructured-modified textiles.


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The results obtained in the creation of new LDH based nanomaterials are certainly encouraging. Nevertheless precise control of chemical composition, morphology and size is still a challenge. Those requirements highlight the need for new characterization techniques to understand the LDHs growth mechanism at a deeper and more comprehensive level, thus promoting the development of new LDHs for high performances applications.

**Composition and structure**

The structure of an ideal Layered Double Hydroxide is based on M(OH)₂ edge-sharing octahedral units forming coplanar brucite-like layers (lamellas) which are stacked on top of one another to form a 3D structures [3-7], as schematically shown in Figure 1. Differently from brucite, which is only formed by neutral magnesium hydroxide, LDH sheets acquire a net positive charge due to the substitution of a certain fraction x of the divalent cations M²⁺ with the trivalent ones M³⁺. These positive charges are balanced by a variety of possible and results reported by various authors, but it should be noted that these structure together. A larger range of 0.15<x<0.5 has been suggested by the electrostatic forces maintain the different layers and the whole 3D structures [3-7], as schematically shown in Figure 1. Differently from brucite, which is only formed by neutral magnesium hydroxide, LDH sheets acquire a net positive charge due to the substitution of a certain fraction x of the divalent cations M²⁺ with the trivalent ones M³⁺. These positive charges are balanced by a variety of possible and exchangeable guest anions intercalated between the lamellas together with water molecules. As a result, a hydrotalcite-like layered structure is formed (Figure 1) which can be represented with the general formula \([\text{M}^2⁺_x\text{M}^3⁺\text{(OH)}_2]_x(\text{An}^-)_n\text{mH₂O}\). There are some constraints for the trivalent to divalent metal ratio x of such a layered structure since the lattice stability requires 0.2<x<0.4. While the upper limit is essentially due to the electrostatic repulsion between neighbouring trivalent cations and the Pauling’s rules, a minimum concentration of M³⁺ is necessary since the consequent charge unbalance must make the electrostatic forces maintain the different layers and the whole 3D structure together. A larger range of 0.15<x<0.5 has been suggested by results reported by various authors, but it should be noted that these values are exclusively obtained by chemical analysis.

**Metallic cations**

LDHs containing various metallic cations have been synthesized with the following divalent cations: Zn, Mg, Mn, Fe, Co, Ni, Cu and Ca, while the trivalent ones are: Al, Mn, Cr, Fe, Co, Ni, and La. LDH-like structure has also been attributed to Li-Al monovalent/trivalent and to Co-Ti divalent/tetravalent couples [3-7]. These lists show that the lattice stability also requires the ionic radius to lie in the range 0.50-0.74 Å. LDHs have also been prepared with more than two different metallic cations, which give the chance of further variations of the chemical/physical properties. For instance, in (Mg₁₋ₓZnx)₂Al-CO₃ Yamaguchi et al. studied the Zn⁺ substitution effects on the structural properties, such as the lattice parameter and interlayer distance, the water content and ionic conductivity [8].

The two metallic cations are generally considered as randomly distributed in the layers on an hexagonal framework and the lattice constant a₀ is a linear combination of the ionic radii and the substitution fraction x. Even though there are some evidence of local ordering of cations, still controversial results have been found demonstrating long-range cation ordering of ordered superstructures [4,9]. Therefore, the use of stoichiometric formulas represents only a simplified formalization in that the studied LDHs are essentially non-stoichiometric even at microscopic level.

**Intercalated anions**

The interlamellar domains of LDHs contain anions, water molecules and, in some cases, other neutral or charged organic/inorganic species. The important characteristics of LDHs is that these moieties are generally weakly bound to the host lamellas and can therefore either be located during the 3D structure formation or be inserted by subsequent substitution trow anionic exchange [10]. The anions can be grouped as follows:

- **Halides**: Cl⁻, F⁻, Br⁻, I⁻, etc.
- **Non-metal oxoanions**: carbonate, nitrate, sulfate, etc.
- **Oxometallate anions**: CrO₄²⁻, MnO₄²⁻, VO₄³⁻, Cr₂O₇³⁻, W₁₀O₃₂⁴⁻, etc.
- **Anionic complexes of transition metals**: Fe(CN)₆³⁻, anionic metal porphyrins, Eu complexes, etc.
- **Organic anions**: --COO⁻, --SO₃⁻, --PO₄³⁻, etc.
- **Anionic biomolecules**: Aminoacids, enzymes, proteins, DNA, TPA, etc.
- **Anionic polymers**: Poly(styrene sulphonate), PMMA, etc.

Neutral molecules have also been intercalated together with anions, possibly with subsequent dissociation in the water contained in the interlamellar domain as in the case of ionic liquids [11], which can be used to control the ionic conductivity of LDHs or for water splitting.

**Interlamellar domains**

Structural characterization techniques, such as XRD and EXAFS, and some physical characteristics of LDHs, such as the behaviour of electrical conductivity and the hydration properties, confirm that the interlamellar domains are in a strongly disordered state which has been considered by some authors as a quasiliquid state [12]. This is also due to the significant presence of water the interlamellar domains. In fact, water in the LDHs is generally distinguished as two general types [13]. The first type is the water bound to the interlayer domains and to the external surface of LDHs even under dry conditions; this one is called crystallite water. The second type is the water adsorbed and desorbed under various temperatures depending on the water vapour pressure and humidity conditions and is called adsorbed water. This variable content of water greatly contributes to the disordered nature of the interlamellar domains and favours one of the most spectacular characteristics of LDHs: the anionic exchange properties. It is, in fact, extremely easy to exchange a great number of interlamellar anions with...
a variety of other ions by simply immersing the LDH synthesized with the "old" anions in a solution with an excess of the "new" anions. As will be discussed in the next chapter, this is an important method for the preparation of novel LDHs. Interestingly, the anionic exchange reaction is revealed by the variations of the interlamellar space, i.e., the distance between two successive hydroxide sheets, which are correlated to the shape and the charge density of the intercalated anions. For instance, in ZnCrZnCr(OH)₂AlH₄O₅LDHs the basal spacing can vary from 0.7 nm to 3.3 nm by changing the intercalated anion A [6]. As a result of this adaptability, LDHs can accommodate even relatively large and complex molecules such as proteins. This interlayer spacing, or more specifically, the interlayer distance d, defined as the thickness of a hydroxide sheet plus one interlayer space, can be easily determined by a series of strong XRD (00l) reflections at low angles, as displayed in Figure 2 which reports the X-ray powder diffractogram of a ZnAlNO₃-LDH. The (110) reflection at high angles, instead, allows the calculation of the lattice parameter a₀, that is the inter-cation distance within the hydroxide layer, while the (01l) and/or the (10l) reflections at intermediate angles enable determining the stacking sequence of the hydroxide sheets, i.e., is the LDH polytype.

**Synthesis Routes of LDH**

LDHs can be synthesized by using a number of techniques and the choice generally depends on the cations forming the hydroxide layers, the intercalated anions and eventually the desired physicochemical properties of the final material e.g. phase purity, crystallinity, porosity, morphology, and electronic and optical characteristics [3-7]. The different methods can be schematically grouped in two main classes: direct methods and indirect ones. Direct methods include: co-precipitation (often coupled with hydrothermal treatment), salt-oxide method, sol-gel synthesis, electrochemical synthesis, and in-situ film growth. Indirect methods, which are rather additional treatments and modifications of pre-synthesized LDHs, comprise: anion exchange, LDH reconstruction, and delamination.

**Co-precipitation**

Co-precipitation, also called salt-base method, was the approach used for the first synthesis of mixed double hydroxides in 1942 [14] and is still the most used method to prepare LDHs. It is often coupled with hydrothermal treatment to improve the crystallinity and the size of LDH particles [15-17]. Basically, it is a low-temperature chemical reaction occurring within water mixed solution of appropriate proportions of divalent and trivalent metal salts in the presence of an alkali metal base at controlled temperature, selected and pH value and under vigorous stirring. The presence of the base causes the simultaneous precipitation of the metal cations in the hydroxide form.

\[
(1-x)M^{2+}A^{q-}_{n/3} + xM^{3+}A^{q-}_{n/2} + 2NaOH + nH_2O \rightarrow M^{2+}_{x}M^{3+}_{1-x}(OH)_{n}A^{q-}_{n/3} \cdot nH_2O + 2NaA^{q-}_{n/4}
\]

Where, A represents the specific anion. Specifically, the reaction produces the condensation of hexaaqua complexes in solution, which leads to the formation of the brucite-like layers with evenly dispersed metallic cations and interlamellar anions. The dispersed LDHs particles, which form in the solution eventually, precipitate producing white slurry at the bottom of the reactor. The precipitate is collected by filtration, then washed and dried in oven. Thermal or hydrothermal treatment can then be performed to improve the crystallinity. The coprecipitation method can be performed either at variable or constant pH, corresponding to high and low supersaturation conditions. In the first case the base solution is progressively added to the mixed solution of divalent and trivalent metal salts. M⁺ hydroxides initially form followed by synthesis of LDHs as further addition of base is performed. Alternatively, in the constant-pH approach, the base solution is added simultaneously with the mixed salt solution carefully controlling the pH value. The latter method permits to achieve a higher chemical homogeneity, provided the pH value is kept constant within the appropriate range determined by the nature of each specific couple of metal cations [5,6]. In general, however, coprecipitation presents the great advantage of providing a direct pathway to prepare an LDH with definite composition. It also offers a high degree of control for synthesis parameters such as temperature, pH, ratio of cations, solution concentration, and aging time. In this way, well-crystallized LDH phases and a good tuning of the M²+/M³⁺ ratio can generally be obtained. Moreover, and most importantly, intercalation of different anionic species in the interlamellar spaces can easily be achieved by using the appropriate counterion in the metal salts and/or by dissolving the specific anionic species, inorganic or organic, in the same water solution of the synthesis [4].

**The salt-oxide method**

The salt-oxide method is basically a solid-liquid reaction between an aqueous suspension of the divalent metal oxide and the aqueous solution of the trivalent metal chloride in excess. This method was introduced in 1977 to synthesize Zn-Cr-Cl LDHs by making a suspension of ZnO react with a 1 M solution of CrCl₃ which was added at constant period of times under vigorous stirring for few days at room temperature [18]. During this slow reaction, the characteristic drops in pH at each addition, quickly recovered to initial value by the buffering nature of the zinc oxide, stops when an excess of chloride does no longer reacts. Since its first use, this method has been extended to Zn-Al-Cl and Cu-Cr-Cl LDHs while attempts with other compositions were unsuccessful [5,6]. In fact, while salt-oxide synthesis generally gives rise to a high degree of crystallinity, it does not make it possible to vary and determine the stoichiometry as much as the co-precipitation method.

**The sol-gel method**

In the sol-gel method, the synthesis of mixed hydroxides starts from the appropriate metal-based alkoxydes and/or acetylatedeoxines, which are used as precursors for a sol-gel transition occurring in water-ethanol solution. The transition is accomplished by a strong acid hydrolysis with HCl or HNO₃. This approach was first introduced in
1996 for the synthesis of Mg-Al-CO\textsubscript{3}, LDHs in the attempt, successfully accomplished, of increasing the M\textsuperscript{3+}/M\textsuperscript{2+} ratio [19]. More recently, the method has been extended to transition metals such as Ni, Cr and Co [20-22] and demonstrated greater thermal stability during calcinations [23].

**Electrochemical deposition**

Kamath et al. in 1994 first achieved electro-deposition of Ni-Al, Ni-Mn, Ni-Cr and Ni-Fe LDH films [24] on the working electrode of a conventional three-electrode setup containing a mixed-metal nitrate bath. This is a one-step technique, recently extended to other metal couples [25-29], which exploits the electrically induced reduction of nitrate ions to produce hydroxide ions on the working electrode with a consequent increase of the local pH value which, in turn, results in precipitation of LDH films. The great interest of this method lies in the fact that it makes it possible the direct deposition, with good adhesion, of LDHs films on metal substrates with a relative control of film density, thickness and morphology. With the conventional chemical methods, instead, the LDH powder obtained from the reaction and the subsequent treatments has to be deposited on the substrate surface with physical methods which do not provide the same reliability and reproducibility of adhesion and morphology. Moreover, electro-deposition of LDHs has demonstrated an effective way to produce modified on electrodes for a huge field of applications in electrochemical sensing.

**In-situ film growth**

This is one more one-step method for direct deposition of LDH films with good adhesion and controllable morphology [30-32]. It could be considered a sort of modified co-precipitation method in that one of the two metals is not provided by the respective dissolved salt but instead by the substrate itself. In fact, the substrate acts both as the reacting source of metal and as a partially sacrificing substrate for the film which grows on it. This approach is even simpler than electrochemical deposition in that it only requires the immersion of the substrate in the water solution of the other metal salt and a base to control the pH value. Moreover, in principle it enables the deposition of LDH films to any surface, provided a thin layer of the reacting metal covers the surface. Most importantly, the surface can be patterned with the thin metal layer so as to form printed circuits with tracks and pads supporting the growth of LDH, which could be very useful for integrated sensors and devices [33]. On the other hand, so far it is still to be demonstrated a good control of the composition and morphology of the deposited film.

**Anion exchange**

This indirect method is based on the fact that the lamellar structure of LDH is highly prone to anion diffusion and exchange. In fact, these properties have been exploited to synthesize new LDH phases by using anionic exchange reactions, which can be described as follows:

$$[\text{M}^{\text{2+}}\text{M}^{\text{3+}}\text{A}]^+\text{B}\rightarrow [\text{M}^{\text{2+}}\text{M}^{\text{3+}}\text{B}]^+\text{A}$$

Where, the equilibrium constant of the reaction depends on the electrostatic interaction and the free energy in a way that ingoing ions with grater charge density are favoured. For instance, for monovalent ions this gives a comparative list of ion selectivity [4,5]: OH\textsuperscript{-}<F\textsuperscript{-}<Cl\textsuperscript{-}<Br\textsuperscript{-}<NO\textsubscript{3}<-F<-I. In practice, stirring an aqueous suspension of the LDH precursors or of the pre-synthesized LDH in the presence of a large excess of the salt of the anion to be intercalated carries out the reaction.

**Reconstruction by rehydration after thermal treatments**

LDHs heated to temperature between 500\textdegree C and 800\textdegree C generally undergo calcination and transform into a solid solution of metal oxides. However, as Miyata et al. [34] found in 1983 in Mg-Al-CO\textsubscript{3}, they can rehydrate with an anion-containing water solution and give rise to a new LDH. More recently, this method has been used to intercalate organic anions [35].

**The delamination/restacking method**

LDHs can be delaminated, i.e. undergo a complete separation of all the component brucite-like sheets, to yield a very stable colloidal solution of mono-dispersed lamellas. If the colloidal dispersion is then gently dried, well-ordered LDHs can be recovered, possibly intercalating different anionic species. Delamination can be performed by a number of methods, especially if organically modified LDHs are used [3,36]. For instance, organic intercalated anions such as methoxide, acetate, for-mate and lactate favour delamination in water [37]. Alternatively, nitrate-based [38] or amino-acid intercalated [39] LDHs can be delaminated in form-amide. By drying, well-ordered LDHs and LDH-polymer Nano composites intercalating a number of organic compounds were obtained [37].

**Applications**

The chemical and physical properties of LDH are currently deeply studied because of their wide range of applications. As it has been pointed out by many review papers [40], LDHs can play significant roles in several different fields, ranging from basic chemistry and pharmacology, medicine, horticulture and environmental remediation to polymeric additive, sensors, surface treatments and industrial fallout.

For an exhaustive treatment of applications such as catalysts and precursors of catalysts, let us refer to the excellent review work of Xu et al. [41] and the references quoted therein.

Therefore within this presentation we will consider significant examples not so much to give a complete picture of possible uses, but to stimulate the curiosity of the scientific community and look for new and challenging applications for these nanostructures.

**Polymeric composites**

To reduce the flammability of plastics it is now impossible, at least in EU, to utilize PBDE (Polynbrominated Diphenil Ether) or PBB (Polybrominated Biphenil), due to the production of toxic by-products connected with their burning process. For this reason halogen free fire retardants have been studied and widely applied. In more recent time LDHs exhibit better properties [42] in flame retardancy. In particular it has been revealed that its decrement is linked to the dispersion of LDH in the polymer matrix, increasing from intercalated LDHs toward exfoliated ones. Evans and Duan [40] prepared a borate-pillared LDH and showed that the intercalation of various anions exhibited a higher smoke suppression. Pereira et al. [43] got a significant flammability reduction of 46\% for an A-LDH (adipate-LDH). For a more complete overview, refer to the paper of Matusinovic and Wilkie [44]. Other possible applications of LDHs in polymers fabrication are in the fields of horticulture to increase the greenhouse effect of cover films [40] and in biomimetics composites [45].

**Biology and medicine**

In the last two decades layered double hydroxides received a great interest also in the field of pharmacology and health. Several papers appeared concerning the intercalation of different anion of pharmaceutical interest [46] such as citrate and silicate. The effects with many others molecules as nucleotides, porphyrin, vitamins, etc.
were considered [47-49]. Due to their biocompatibility [50] LDHs can be used in medicine as excipient [51], or for drug delivery, with a PH dependent releasing rate [52,53]. Also intercalation of antibiotics has been widely studied [54] as well as of DNA molecules for cancer therapy. In this case it is crucial to dispose of a vector, either viral or non-viral, to introduce DNA into cells [55]. Leroux et al. succeeded in adopting LDH as gene carrier of As-myc oligonucleotides [56]. If As-myc is transported by LDH, it can penetrate the cell. Almost 65% of HL-60 cells growth is inhibited.

Cunha et al. [57] presented another interesting application. They studied the biocompatibility of the material by in vivo tests on rats. They implanted a tablet of Mg-Al-Cl and Zn-Al-Cl LDHs, with chloride intercalated ions, into abdominal walls. After 28 days no inflammation was present, neither an increase of tissue volume. These results indicated that LDH tablets determined no antigenic reactions.

In biosensing, LDHs were adopted several times to activate electrodes in simple, low cost and sensitive chemical sensors. They can be classified as "amperometric" if the measured signal is a current, "conducimetric" if it is an impedance/conductance, "potentiometric" in the case of a voltage. LDH/modified electrodes have been applied to detect glucose, haemoglobin, and codeine [58-60].

"Conducimetric" if it is an impedance/conductance, "potentiometric" can be classified as "amperometric" if the measured signal is a current, "conducimetric" if it is an impedance/conductance, "potentiometric" in the case of a voltage. LDH/modified electrodes have been applied to detect glucose, haemoglobin, and codeine [58-60].

It is evident that the combination of organic-inorganic composite, as polymer-LDH, offers a great potentiality in electro-analytical applications due to its structural and/or functional behaviour. For a comprehensive list of patents [61].

Catalysis

The possibility to engineer LDHs at atomic and molecular level has an enormous consequence for science and technology. This is linked, as underlined previously, to the particular properties of the materials, as solubility, ion exchange, thermal conversion, intercalation, etc. [62].

In the previous paragraphs we already encounter some catalytic use of LDHs. What will be stressed in this section is linked to more specific applications of the phenomenon to build up devices in different field: energy conversion and storage, water splitting, environmental remediation, soil conditioning, waste water treatment, VOC (Volatile Organic Compound) decomposition, super capacitor.

Photo catalytic performances are connected to the semiconductor peculiarities: band gap, charge separation, charge mobility. Nanoscale LDH sheets seem to be an ideal solution, due to the possibility of manipulating and controlling composition and defects.

Water splitting: One of the main field in which photo catalysis is applied is the generation of H2 and O2 by water splitting, using solar radiation.

Zn-based and Ti-based LDH were considered since they exhibit visible light activity. Nevertheless their activities are still too low because of the long migration path and the big dimensions of the particles. For this reason nanosheets of LDH have attracted attention thanks to their specific surface area, the higher number of active sites and the shorter path the charges must travel [63].

It was also demonstrated the possibility of improving the efficiency of LDH nanosheets by coupling them with other semiconductors. Better absorption range and better charge transfer separation was obtained [64-66]. Feng et al. [67] recently propose a simple synthesis of a CoFe layered double hydroxide, with high activity and stable oxygen evolution.

VOCS remediation: Volatile organic compounds (VOCs) represent a crucial factor for environmental pollution. One the best effective treatment is the catalytic combustion. The LDH precursor can be adopted to prepare mixed oxides. Several works appeared in which LDH performances are examined relative to the total combustion of common VOCs, such as ethanol, methane, and toluene [68-70].

In organic wastewater treatment, layered double hydroxides succeed in removing organic compounds. Recently, since sunlight can be used as energy source, solar light driven catalyst has been developed. Shu et al. [71] derived NiTi-mixed oxide from NiTi-LDH precursor. In another study, coating Fe3O4 particle surface formed a core-shell structure by LDH particles. This magnetic catalyst exhibited high photovoltatic activity under visible light mitted by a pressure mercury lamp [72].

Environmental problems heavily derive from the emission of NOx and SOx into the atmosphere. Those gases are responsible of greenhouse gas effect, acid rains, smog.

NOx is normally removed in three ways: - direct decomposition; -selective catalytic reduction; -storage and reduction. For SOx transfer catalysis is adopted [73-75].

Energy storage and conversion: Energy is probably the most important topic of the century. Therefore the need not only of renewable energy, but also of energy storage systems is mandatory. To this aim super-capacitor and ion battery represent a reasonable answer. For all these devices, the most important components are the electrodes. Therefore the best way to reach the goals is to realize new electrodes with special structure, such as nanorods, nanowires and nano-sheets.

Delaminated LDH was first used to fabricate a thin film electrode in 2007 [76]. It was demonstrated that this film had good supercapacitor behavior with a high specific capacitance, good electrochemical stability, and a high-rate capability.

Many other materials can be considered as supercapacitor like carbon-based materials (carbon nanotubes, carbon gels, graphene oxides, etc.). To realize better electrodes is therefore suitable to consider carbon materials/LDHs composites. Applications of these types have been considered since 2006 [77].

Inorganic semiconductor and organic sensitizer have been widely used in solar cells due to efficiency, easy production and low cost [78,79].

Quantum dots and perovskites are inorganic sensitizer applied to photovoltaic cells to enhance their low stability and narrow absorption band. It is possible to improve the harvesting ability of the dye by hybridizing it with nanosize materials as LDH since it gives higher heat stability, photo stability and is environmental friendly [80].

Anti-corrosion: The realization of LDH films with controlled architectures is desirable for functional coatings. What is of particular interest is the possibility to realize large-area LDH films to face corrosion problems [81-83]. Recently, layered double hydroxides have been used to immobilize or encapsulate corrosion inhibitors, such as 2-mercaptopentobenzothiazole (MBT), promoting their controlled release in a more eco-friendly way.

Their host structure acts as a scavenger towards aggressive ions (e.g. Cl-). Conversely Cl- ions have good affinity with LDH materials. The entrapment is associated by displacing the interleaved anion, i.e. the corrosion inhibitor, if the ion exchange reaction proceeds. As remarked LDH host structure is able to load different anions,
inhibition efficiency of intercalated inorganic or organic anions such as, for example, carbonate [84], vanadate [85], and molybdate [86].

Also ceramic-like coatings formed with PEO (plasma electrolytic oxidation) make possible real improvement of the mechanical properties and corrosion resistance of Al alloys which can therefore be used more widely, hence providing low weight structures [87,88].

The process implies the polarization of the Al alloy to voltage value higher than the dielectric breakdown. The treatment is developed in environmentally friendly dilute electrolytes and causes plasma micro-discharges across the growing oxide. At the end the coating is a mixture of substrate metal oxide and other complex oxides involving components inside the electrolyte [89]. Recent developments for PEO coated Al alloys concentrated on preparing surfaces suitable for new multifunctional applications. Ad hoc PEO coatings can be achieved in one step, modifying the composition of the electrolytes [90,91] and process parameters [92]. A two-step process is neutralized by a suitable post-treatment [93-95]. Those treatments have to increase the corrosion resistance of PEO, due to the porous structure. In any case presence of cracks and other defects reduce the service life. The LDH structure played a fundamental role in this situation too. It permitted to contain corrosion on Al and Mg alloys by encapsulating inhibiting compounds [96-99].

Alumina refinement: To remove heavy metal ions and organic species from wastewaters, as in the Bayer process, LDHs have been adopted taking advantage of the lamellar structure, the adjustable distances between layers and the interlayer reactivity [99,100]. The liquid component of the “red mud” requires neutralization. The most common practice consists of adding Mg-rich seawater, which results in the formation of precipitates containing Mg and Al [101]. These precipitates are in hydrotalcite form [102]. Together with this “unintentional” LDH formation [103], they can also be produced intentionally in the refinement process. Several studies were developed toward this direction. To mention just some of them, we remind the works of Nigro and O’Neill [104] who investigated the use of hydrotalcite in the removal of coloured impurities. Perotta and Williams revealed the reduction of oxalate in liquor, due to the formation of hydrocalumite at temperatures up to 60°C.

In parallel with the water treatment, the formation, intentional and/or unintentional, of LDH allows the recovering of alumina values from the first liquor, by means of a modified version of the Bayer’s process. It is essentially divided into three steps: a) addition to the liquor of a metal which reacts to form an Al-LDH, in such a way that the resulting aluminate ion concentration within the liquor is smaller than the initial one; b) processing of the Al rich LDH by, for example, a solution of carbonate ions, which provides both aluminate ions, and an insoluble salt of metals different from aluminium. This can be further treated to “rebuild” the LDH material; c) directing the liquor with high aluminate ion concentration to the alumina refinery [105,106].

Controlled Film Deposition

In the last decade, different groups [30-32] have demonstrated that LDH films can be deposited on metal surfaces by using aluminium or zinc foils as sacrificial substrates for the in-situ growth that is a sort of modified coprecipitation method as described in paragraph 1.3.5. Those studies were mainly addressed applications of LDHs as anticorrosion coatings or functionalized electrodes for electrical batteries and capacitors. More recently, our group has demonstrated that controlled films can also be grown an aluminum thin films, which were previously sputtered or evaporated on any surface [33,107]. In this way, LDHs films made of lamellar-like nanoplatelets, can be grown selectively on specific areas, with submicrometric-level resolution (about ±0.5 μm), by prepatterning the aluminum layer with conventional photolithographic techniques (Figure 3). This strategy represents a necessary starting point for implementation of possible LDH-based devices and sensors in miniaturized electronic chips. Moreover, while the general morphology of the films was quite invariant against the experimental conditions, with intersecting nanoplatelets mainly oriented perpendicular to the substrate surface, the number density and thickness of each nanoplatelet could be varied by changing the intercalated anion (Figure 4). Moreover, with a single intercalated anion, the thickness of each nanoplatelet tuned by controlling the thickness of the predeposited aluminum layer (Figure 5). Preliminary studies have also been carried out to implement modified biosensors (Figure 6) and to impregnate paper or cotton fibers with LDHs in order to prepare functionalised filters or make flame retardant textiles (Figure 7).

Figure 3: (a) Particular of a single LDH micro/nanoresistor deposited onto an aluminum thin film with a thickness of 300 nm; (b) zoom of a LDH micro/nanoresistor deposited onto an aluminum thin film with a thickness of 300 nm.

Figure 4: Low-magnification: (a and b) high-magnification, (c and d) SEM images of Zn-Al LDHs grown onto Al thin layers with: Cl, (a,c) SO3--; (b,d) intercalated anion.

Figure 5: High-magnification SEM images of Zn-Al LDHs grown onto Al thin layers with a thickness of: a) 100 nm and b) 25 nm; c) the thickness of the LDH nanoplatelets as a function of the thickness of the aluminum layer.
Conclusion and Perspectives

This review highlights only some of the progresses in applications of Layered Double Hydroxides nanostructures, within the areas of catalysis, electrode materials, polymer nano composites, bioinorganic hybrid materials, bio-med applications, etc. As it was stressed several times, LDHs exhibit great potential, thanks to their great flexibility. However, despite the many recent advances described here, opportunities and challenges remain either in fundamental or applied research on LDHs.

Looking ahead, efforts are still needed to design and synthesize low cost and high quality LDH based materials to meet requirements of applications.

These include controlling the chemical composition, size and morphology; meanwhile, it is also important to make the synthesis processes greener and more environmental benign.

The possibility to isolate delaminated nanosheets from dispersion, without causing aggregation, is still difficult to realize. Near future development will regard functionalization of LDH shells, due to their simple fabrication. For the same reasons, successes can be expected in the field of ultrathin films from delaminated LDHs. Anyway great attention must be paid to the choice of the proper layered double hydroxide and to corresponding substituted and intercalated anions.

Nevertheless, important fields will be, for sure, the medical and pharmaceutical ones, either for the synthesis of new biosensors or for the development of new formulations for drugs and cancer therapy.

All these studies will take on a crucial value for LDH-based materials to have a disruptive impact in the most different arenas in the next and far future.

References


