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LAYERED DOUBLE HYDROXIDES AS FUNCTIONAL MATERIALS AND THEIR TECHNOLOGICAL APPLICATIONS

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Abstract: Layered double hydroxides (LDHs) have fascinated materials chemists due to their wide variety of applications in various fields. The unique property of layered double hydroxides is their interlayer spacing that entertain the intercalation and deintercalation variety of anionic species. Organic pharmaceutical drugs have been intercalated into the interlayer galleries of LDHs and, consequently, novel nano drugs or smart drugs have revolutionized the medical field. LDHs, as green nanoreservoirs with sustained drug release and cell targeting properties hold great promise of improving health and prolonging life. LDHs are employed for the sorption of heavy and toxic metal ions, CO_2 sequestration, electrode materials, materials of supercapacitors, polymer additives, photocatalysts, heterogeneous catalysts etc., This chapter focuses on the general discussion of the synthesis, characterization and applications of LDHs in various fields of research concern.

Keywords: Layered double hydroxide, Ion exchange

Layered double hydroxides (LDH) are known to material chemists for the past 150 years. Hydrotalcite was determined stoichiometrically by Manasse for the first time in 1915 [1-2]. However in 1960 the complete structure of hydrotalcite was investigated by X-ray diffractometry. Since then, these materials have fascinated researchers due to their wide application in various fields of current concern. This article is intended to review the recent technological applications of LDHs

Layered double hydroxides (LDH) forms an important class of inorganic materials owing to their applications in the wide area of current research. Layered double hydroxides are obtained by partial isomorphous substitution of divalent metal ions by trivalent metal ions in the structure of mineral brucite, Mg(OH)2. Their chemical composition can be expressed by the general formula MII1-xMIIIx(OH)2An-x/nyH2O, where MII and MIII are divalent and trivalent metal cations and An- is an n-valent anion. These compounds have a layered crystal structure composed of positively charged hydroxide layers

$[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}$ and interlayers containing anions and water molecules. The value of x represents a portion of trivalent metal cations substituted in hydroxide layers and usually corresponds to $0.20 < x < 0.33$[3-4]

Layered double hydroxides exhibit anion-exchange properties, i.e., anions in the interlayers may be exchanged for the other ones. At temperatures of approximately 300 – 500 °C, layered double hydroxides are decomposed to form mixed oxides of MII and MIII metals. In Rehydration of these mixed oxides takes place in anaqueous solution containing the anion to be intercalated, resulting in the reconstruction of the layered LDH structure along with the intercalation of anions from the solution into interlayers [5]. This unique property of layered double hydroxides can be employed for preparation of compounds intercalated with various anions or in removal of anions from solutions. The often used group name "hydrotalcite-like compounds" is related to the mineral hydrotalcite ($Mg_6Al_2(OH)_{16}CO_3\ 4H_2O$). There are some other natural minerals and a great number of synthetic compounds with an analogous layered crystal structure combining various MII and MIII metal cations in hydroxide layers and various anions intercalated in the interlayers.

Layered double hydroxides are consumed in the plastics industry. Synthetic hydrotalcite is used as a neutralizing agent (acid scavenger) in production of polyolefins and as a component of PVC stabilizing compositions [6]. Layered double hydroxides can be applied also as nanofillers for synthesizing polymer-based nanocomposites [7], in which inorganic nanoparticles dispersed in relatively low concentration in the polymer matrix improve its properties. The representative pharmaceutical application of layered double hydroxides is the hydrotalcite-derived antacid but they are also tested as carriers for drugs and other bio-active substances (for example, non-steroidal anti-inflammatory drugs, vitamins, DNA fragments, etc.) [8-11]. Layered double hydroxides are widely used in heterogeneous catalysis, mainly as precursors for preparation of mixed oxide based catalysts. The anion-exchange properties of layered double hydroxides and their ability to recover the layered crystal structure during rehydration of thermally decomposed products may be utilized for adsorption of undesirable contaminants [12]. Layered double hydroxides represent also a host inorganic structure suitable for intercalation of various anions resulting in the preparation of hybrid materials with interesting physical and chemical properties [13].

Synthesis of layered double hydroxides

Layered double hydroxides can be synthesized by urea hydrolysis, solid state reaction, co-precipitation, and hydrolysis of salts and oxides techniques.[13 a.]

1. Co-Precipitation Method

The co-precipitation technique is the most commonly used and simplest method. A solution containing the anion guest is added to an aqueous solution of two different metals that are used as precursors. This is followed by drop-wise addition of an alkaline solution to the mixture under vigorous stirring and a nitrogen atmosphere until a final pH of 7–10. The mixture is aged at 70 °C for 18 h and the resultant slurry is then filtered, washed with water, and finally dried in an oven at 60 °C. This method produces large quantities of nanocomposite and the packing density of the interlayer anion is diverse due to variable M^{+2}/M^{+3} ratios. Furthermore, a wide diversity of anions can be incorporated between the layers. However, there is a significantly higher uptake of carbon dioxide and incorporation of unwanted hydroxide anions from the reaction mixture [13-15].

Precipitation at High Supersaturation

The precipitation at high supersaturation method requires the addition of a mixed metals salt solution to an alkaline solution that contains the interlayer anions. The materials that are synthesized by this method usually have low crystallinity, and therefore thermal treatment or aging is used after co-precipitation to increase the crystallinity of the materials [16].

Precipitation at Low Supersaturation

Precipitation at low supersaturation is accomplished by slow addition of mixed solutions of divalent and trivalent cation metal salts to an aqueous solution of the interlayer anion. The alkaline solution is added simultaneously to maintain the pH at selected value to lead to co-precipitation of the two metallic salts. This method gives LDHs with high crystallinity and allows control of the molar ratio, $R = M^{2+}/M^{3+}$.

2. Ion Exchange Method

When the metal cations or intercalated anions are unstable, the co-precipitation method is not applicable for the encapsulation procedure. Therefore, in these cases, the ion exchange method is useful. A solution containing anionic guest is added to 50 mL of an aqueous solution containing the LDH. The pH of the reaction mixture is kept at 7–10 by simultaneous addition of an alkaline solution and the suspension formed is magnetically stirred vigorously for 3 h. The slurry is aged at 70 °C for 18 h and then filtered, washed with decarbonated water, and dried in an oven at 60 °C. In this method, the guest anions are exchanged with the anion present in the interlayer space [17].

The ion-exchange process may be affected by some factors namely:

a. Incoming anion affinity.

The ion exchange process will be alleviated if the incoming anion has a higher charge and smaller size (smaller ionic radius) [18].

b. Exchange media

The organic solvent favors the exchange by organic anions, whereas the aqueous medium favors the exchange by inorganic anions [19].

c. pH value

pH value affects the interaction between the LDH layers and interlayer conjugated base anions. At low pH, this interaction is weak because the LDH is not stable in acidic media (lower than pH 4) and this will result in the fact that the LDH dissolves.

d. Chemical composition

The hydration state and charge density have an effect on the ion-exchange process and the charge density and hydration state of the LDH's interlayer can be affected by the chemical composition of the layers in LDH [20].

3. Hydrothermal Method

The hydrothermal method is usually used during the preparation or intercalation process to control particle size and size distribution in order to produce LDHs with uniform size and high crystallinity [21].

4. Urea Hydrolysis Method

Urea has some excellent features and can be used as a precipitation agent. The LDH prepared by this method has homogeneous sizes and platelet-like primary particles with well-defined hexagonal shapes and good crystal quality [22].

5. Reconstruction/Rehydration Method

This method involves calcination and regeneration of LDHs. In LDH calcination, removal of the water interlayer and anions, and dehydroxylation of the layer occurs, resulting in the formation of a metal oxide. In addition, exposing the metal oxide mixture to water and anions leads to regeneration of the layer structure. At the end, anions intercalate into the interlayer gallery and water reforms the hydroxyl layers [23].

6. Electrosynthesis

The author has used electrogeneration base technique for the synthesis of Mg-Al- LDH [24].

Characterization of Layered Hydroxides

The most common analytical techniques used to characterize layered double hydroxides arePowder X-ray diffraction (PXRD), Fourier transform infrared (FTIR) spectroscopy,thermogravimetric analyses (TGA/DTG), Scanning Electron Microscopy (SEM) and Transmission electron microscopy (TEM). Powder X-ray diffraction is used to determine purity, crystallinity, and the basal spacing of the LDHs. FTIR spectroscopy is used to identify the functional groups and chemical bands, because each functional group has its own specific wavenumbers and characteristic absorption peaks. Therefore, FTIR can be used as a supporting technique to confirm that intercalation has occurred instead of absorption. The chemical composition of the LDHs is analyzed for metal ions by inductively coupled plasma atomic emission spectrometry. The thermal stability of LDHs is measured using thermogravimetric and differential thermogravimetric analyses while the surface characterization of the LDH is carried out using surface area analysis. Scanning electron microscopy is used to determine the surface morphology of the LDHs. Optical properties and the controlled release studies are accomplished using an ultraviolet-visible spectrophotometer. Transmission electron microscopy (TEM) is used for particle size determination of layered hydroxides.

The fundamental structure of the LDH in a three dimensional view would look like[25],

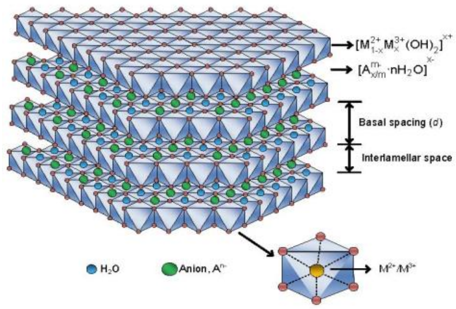


Fig.1& 2 Structure of an LDH in 3-D

Jairo Tronto, Ana CláudiaBordonal, Zeki Naal and João Barros Valim Materials Science » "Materials Science - Advanced Topics", book edited by Yitzhak Mastai, ISBN 978-953-51-1140-5, Published: June 10, 2013 underCC BY 3.0 license. © The Author(s).

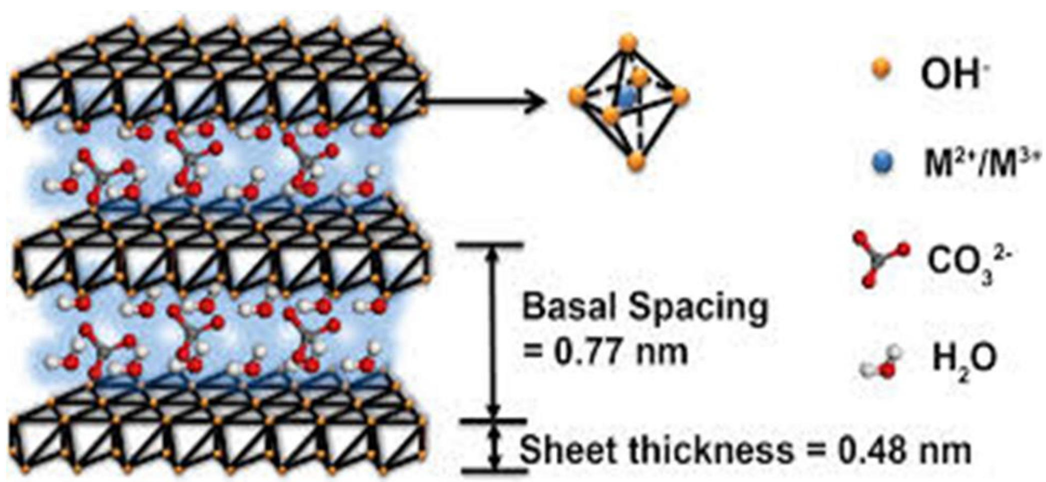


Fig. 2

The powder X-ray diffractogram for a typical crystalline LDH is as shown in the fig 3

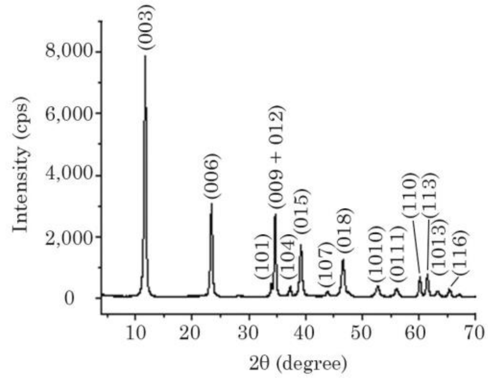


Fig.3X-ray powder diffractogram of a ZnAl-NO3-LDH. Source: Tronto (non-published data). Rev. Bras. Ciênc. Solo vol.39 no.1 Viçosa Jan./Feb. 2015

The PXRD pattern for the LDHs show sharp, symmetric, and intense lines at low 2θ values and less intense and generally asymmetric lines at higher 2θ values. The reflections due to (003) (006) and (009) clearly shows that it is a layered material. The interlayer spacings (d) can be calculated by using the Bragg's equation 2d sinθ= nλ. The sharp intense lines and a doublet peak at a 2θ value of 60° indicate the existence of an ordered layered material [26]**.**

IR Spectra of LDHs

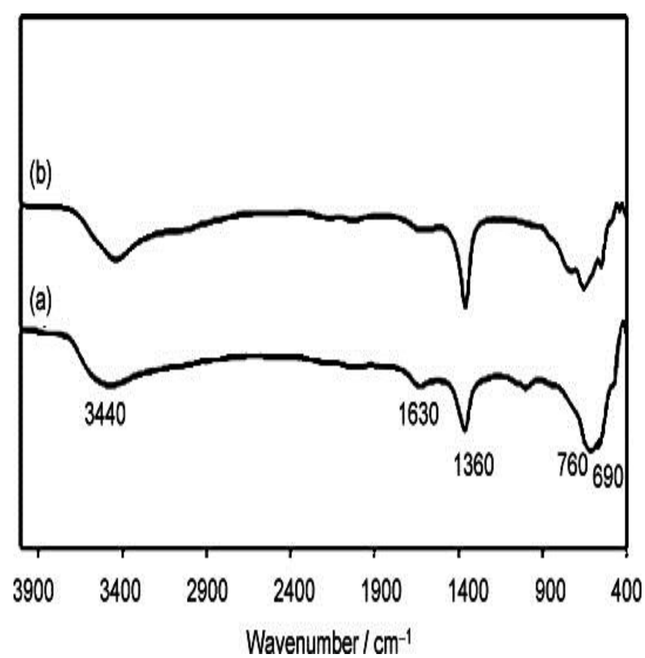


Fig. 4 FT-IR Spectra of LDHs

The infrared (IR) spectra of Mg−Al andMg−Al:DNA are shown in Figure 4 . A broad peak at 3395–3450 cm−1 and a weak one at 1636–1367 cm−1 correlate to ν(OH) and δ(H_2O) bands respectively. Peaks at 650–665 cm−1 and 410–446 cm−1 are due to M−O vibrations and M−O−H bending, where M=Mg and Al. The sharp singlet observed at 1300–1362 cm−1 is due to the stretching of the carbonate ion [27].According to Valcheva–Traykova et al., sharp peaks at 446 cm−1 and 1352 cm−1, doublet peaks at 769 cm−1 and 661 cm−1, and a broad peak at 3396 cm−1 are all characteristic of an LDH structure [28].

Thermogravimetric analysis

Thermal decomposition of Mg-Al-LDH is involves three steps dehydration, dehydroxylation (loss of lamellar hydroxyls) and loss of interlayer carbonate. Figure 5 shows the results of thermal analysis for LDH MgAl-CO_3. The steps and sequence of thermal decomposition of LDHs can vary with the ratio of cations, (Hibino et al., 1995[29]) but generally follow the same sequence. The first transition temperature and mass loss, below 200 °C, is associated with the evaporation of adsorbed and intercalated water molecules. The other steps, between 200 and 500 °C, refer to the decomposition of interlayer carbonate and hydroxyl groups of the lamellae (Hibino et al., 1995). Above 500 °C, the lamella of the brucite-type structure collapses and a solid solution of mixed spinel ($MgAl_2O_4$) and MgO, or Al_2O_3 and MgO is irreversibly formed. The first mass-loss shown in Figure 2 indicates that the synthesized material has 0.058 mol of water per unit of hydrotalcite, implying that its structural formula is $[Mg^{+2}\ 0.67Al^{+3}\ 0.33\ (OH)_2]^{+0,33}\ CO_3^{-}.0.058H_2O$[29].

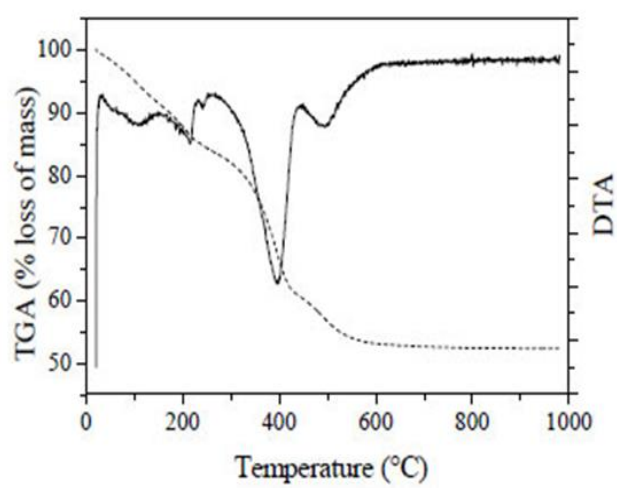


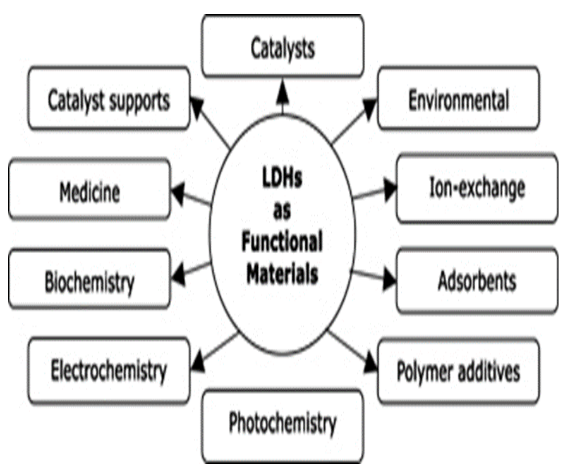
Figure 2: Thermal analysis of the synthesized LDH.

Surface area of LDHs

The specific surface area of LDH may reach 100 m2/g, and the values found in this study (10.7 m2/g for LDH and 21.2 m2/g for calcined LDH) were compatible with the range of values normally observed in the literature (Crepaldi et al., 2002 [30]). In addition, the pore sizes of the synthesized materials were 23 nm, for LDH, and 15 nm, for the calcined LDH, classifying both materials as mesoporous. The calcination leads to a greater number of micropores, resulting in a considerable increase in the surface area. This increase could be related to the formation of channels in the material during the evolution of water vapor and carbon dioxide (Cavani et al., 1991[13]). The nitrogen adsorption/desorption isotherm (data not shown) indicated no hysteresis, thus suggesting the presence of cylindrical pores with open channels.

LDHs have anionic exchange capacity, and the ability to capture organic and inorganic anions makes them almost unique as inorganic materials. LDHs are extensively used in catalysis, ion-exchange, adsorption, pharmaceutics, photochemistry and electrochemistry; catalysts, electrode materials etc., since the hydroxide layers are positively charged a variety of anions can be intercalated. Intercalation and controlled release of pharmaceutically active compounds from a layered double hydroxide is a breakthrough in the area of medicine. LDHs acts as biocompatible delivery matrix for drugs and facilitates a significant increase in delivery efficiency.

The various applications of layered double hydroxides as functional materials in the area of current research are listed as follows[31].



Sorption of toxic metal ions

Dermat O'Hare and etal., have used Li-Al LDH for the sorption and removal of heavy metal ions. LDHs owing to their significant interlayer spacing can act as a very sorbing agents for heavy and toxic metal ions like Cr(VI), Cu(II), As, and Se, which is very useful in industrial effluent treatment systems. Hexavalent Cr has been identified as one of the toxic metals commonly present in industrial effluents. Among the treatment techniques developed for removing Cr(VI) from waste waters, sorption is most commonly applied, due to its simplicity and efficiency. However, few adsorbents can be recycled and reused cost-effectively. The removal of Cr(VI) by Li/Al LDH was evaluated in a batch mode. The results demonstrated that Cr(VI) adsorption onto Li/Al LDH occurs by replacing the Cl- that originally exists in the interlayer of the adsorbent. The degree of Cr(VI) adsorption observed for Li/Al LDH was relatively high and the process occurred rapidly; however, a portion of adsorbed Cr(VI) was gradually desorbed, due to the Li de-intercalation of Li/Al LDH.. That is, Li/Al LDH may be used as an effective adsorbent for the adsorption of Cr(VI) in an ambient environment[32].

LDHs for CO_2 sequestration

Atmospheric concentrations of several greenhouse gases, in particular, carbon dioxide (CO_2) have increased significantly in the recent past largely due to the combustion of fossil fuels. The capture of CO_2 from industrial flue gases has therefore become a vital issue attracting the attention of several research groups and organizations in the world. One of the important options to control CO_2 emissions is carbon dioxide sequestration that is, capturing and securely storing CO_2 emitted from major sources of emission. There are several existing options available for CO_2 capture however, each of these systems has its own limitations that impede the technical or economical viability in CO_2 post combustion capture systems. Selective adsorption mechanism is a promising technique considered for CO_2 separation. A few inorganic materials (zeolites and activated carbons) were found to have good adsorption capacities of CO_2. However, they are not attractive for separation from wet feeds at high temperatures due to poor hydrothermal stability. Layered double hydroxides (LDHs) are novel inorganic compounds, and in particular their layered double oxide (LDO) derivatives produced on calcination have desired properties as CO_2 adsorbents in post-combustion capture applications [33-34].

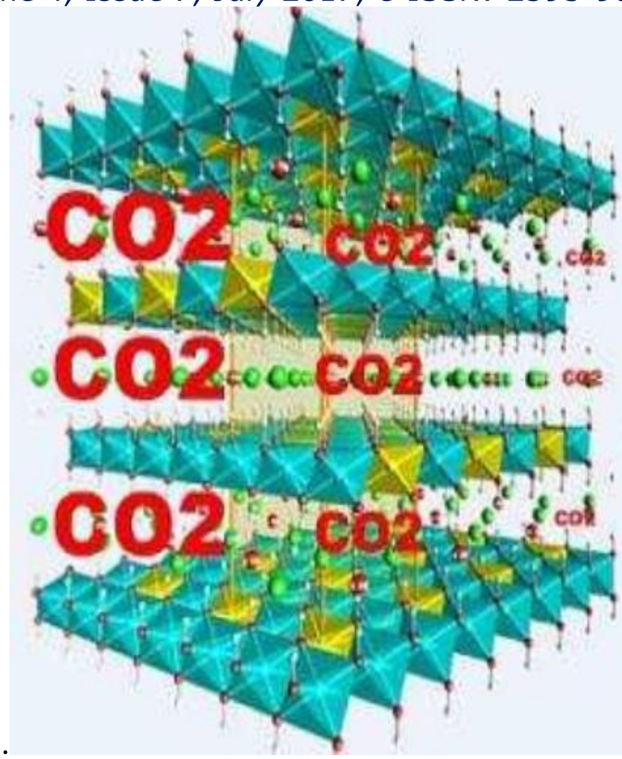


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Fig.6 CO_2 sequestration by LDHs By Lee Swee Heng

LDHs as electrode materials

Nickel-based layered double hydroxides (LDHs) having the composition

Ni1-xMxIII$(OH)_2$(An-)x/n·zH_2O (x=0.2–0.33, MIII=Al, Fe, Co) are isostructural with α-nickel hydroxide. The LDHs of Ni with Cr and Mn are also electrochemically active and deliver capacities of 400-500 mAh g−1 of Ni [35].

An innovative strategy of fabricating electrode material by layered assembling two kinds of one-atom-thick sheets, carboxylatedgraphene oxide (GO) and Co-Al and Ni-Co layered double hydroxide nanosheet (Co-Al LDH-NS) for the application as a pseudocapacitorare reported. The Co-Al LDH-NS/GO composite exhibits good energy storage properties.Ni-Co LDH hybrid film-based electrodes display a significantly enhanced specific capacitance (2682 F g−1 at 3 A g−1, based on active materials) and energy density (77.3 Wh kg−1 at 623 W kg−1). The asymmetric supercapacitor, with the Ni-Co LDH hybrid film as the positive electrode material and porous freeze-dried reduced graphene oxide (RGO) as the negative electrode material, exhibits an ultrahigh energy density (188 Wh kg−1) at an average power density of 1499 W kg−1 based on the mass of active material [36-37]

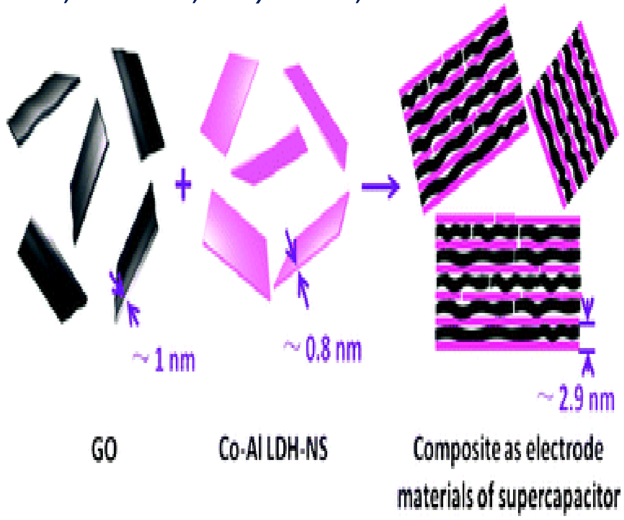

Fig.7 Graphical abstract: Layered assembly of graphene oxide and Co–Al layered double hydroxide nanosheets as electrode materials for supercapacitors

Layered double hydroxides as polymer additives

Layered double hydroxides (LDH), a class of anionic clay materials, were developed as an effective additive for polymer gelled electrolytes for use in dye-sensitized solar cells (DSSC). Carbonate and chloride intercalated Zn-Al LDHs, Zn-Al-CO_3 LDH, and Zn-Al-Cl LDH were prepared with coprecipitation methods. The addition of the LDHs significantly improved, in terms of power conversion efficiency (PCE), over the plain poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) gelled electrolyte and competed favorably with the liquid electrolyte based DSSCs, 8.13% for the liquid electrolyte, 7.48% for the plain PVDF-HFP gelled electrolyte, 8.11% for the Zn-Al-CO_3 LDH/PVDF-HFP gelled electrolyte, and 8.00% for the Zn-Al-Cl LDH/PVDF-HFP gelled electrolyte based DSSCs. The good performance in PCEs achieved by the LDH-loaded DSSCs came mainly from the significant boost in open circuit voltages (Voc), from 0.74 V for both the liquid electrolyte and PVDF-HFP gelled electrolyte based DSSCs to 0.79 V for both the Zn-Al-CO_3 LDH/PVDF-HFP and Zn-Al-Cl LDH/PVDF-HFP gelled electrolyte based DSSCs [38].

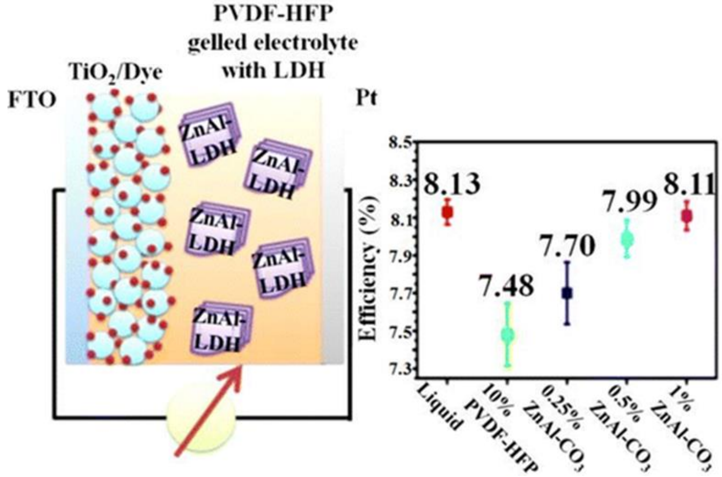

Fig. 8 LDH as additive in polymer gelled electrolyte

LDHs as efficient photocatalysts

Oxygen generation through photocatalytic water splitting under visible light irradiation is a challenging process. A series of Zn/Ti, Zn/Ce, and Zn/Cr LDH have been synthesized and used as photocatalysts for oxygen generation from water. These quantum yields are among the highest values ever determined with visible light for solid materials in the absence of light harvesting dye. The overall efficiency of (Zn/Cr) LDH for visible light oxygen generation was found to be 1.6 times higher than that of WO_3 under the same conditions [39].

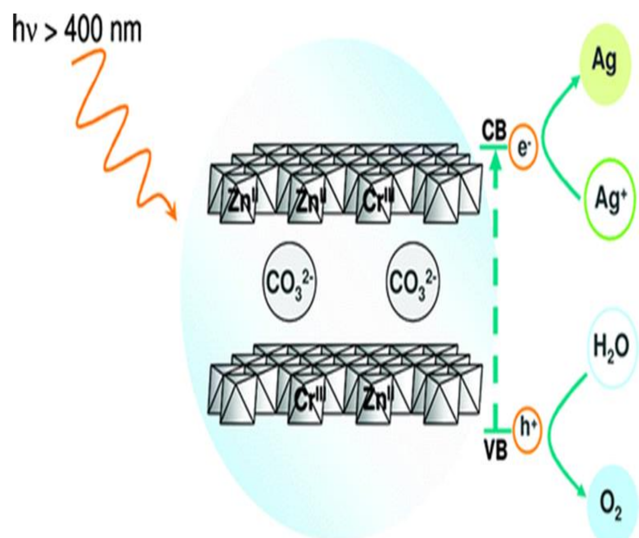

Fig.9 Zn-Cr-LDH photocatalyst for Oxygen generation

LDHs as good heterogeneous catalysts

LDHs are very good heterogeneous catalysts. Development of effective and recyclable water-tolerant catalysts, especially heterogeneous catalysts, is the main challenge for the catalytic reactions in aqueous medium. Layered double hydroxides (LDHs) are a class of anion clays consisting of brucite-like host layers and interlayer anions, with versatility in composition, morphology and architecture. By virtue of the hydrophilicity of the hydroxyl-riched host layers as well as the 2D confined region of interlayer gallery, LDHs display great potential as supports to immobilize catalytically-active species so as to obtain water-compatible heterogeneous catalysts, in which catalytic sites can be preferentially orientated, highly dispersed, and firmly stabilized to afford excellent catalytic performance and recyclability in aqueous medium. Moreover, LDHs can be used as precursors for the preparation of hydrophilic metal or metal oxides catalysts based on the unique topotactic process transformation [40].

LDHsdue to the flexible tunability and uniform distribution of metal cations in the brucite-like layers and the facile exchangeability of intercalated anions, LDHs—both as directly prepared or after thermal treatment and/or reduction—have found many applications as stable and recyclable heterogeneous catalysts or catalyst supports for a variety of reactions with high industrial and academic importance [41]. A major challenge in this rapidly growing field is to enhance the activity, selectivity and stability of these LDH-based materials by developing ways of designing the electronic structure of the catalysts and supports.

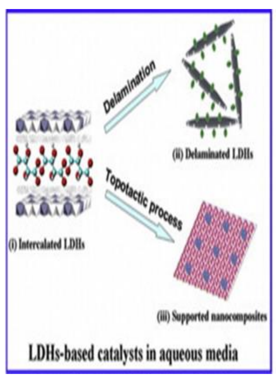

Fig. 10

LDHs in drug delivery

The unique structure of LDH consisting of an outer positively charged metal hydroxide sheets and inner interlayer anions hydrated with water molecules favors in its uptake and cellular penetration [42]. A controllable anion exchange that is pH dependent is possible due to the fascinating structure of LDH, which is also the basis of controlled-release properties of this carrier, making it a valuable choice for biological and pharmaceutical applications [40]. In the field of biomedical application, different types of LDH were exploited for drug delivery, although they are still in the preliminary stage, but the results are promising.

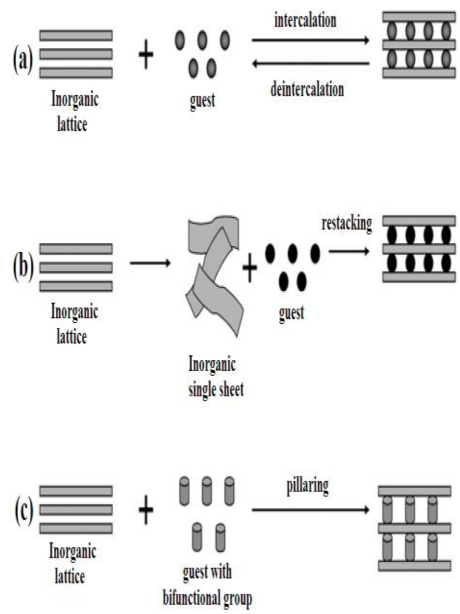

Fig. 11 Reaction routes to incorporate biomolecules into layered nanomaterials

(a) intercalation; (b) exfoliation-restacking; (c) pillaring reaction.

LDHs are emerging as potential new drug delivery system due to its low toxicity and higher biocompatibility [41-42]. Some studies have shown LDH to have the same or lower toxicity than the corresponding pure drug it carries when tested on normal cell lines [41-42]. The controlled, sustained and pH dependent release property of LDH is making it biocompatible to most tissues, cell and animals as a whole. As exciting as the toxicity evaluation results of most synthesized LDH are, their application especially in drug delivery may be hindered by lack of standardization of physicochemical parameters. The toxicity potential of many drugs were significantly reduced after intercalation into either zinc or magnesium LDH nanocomposite. Drug efficacies including anti-cancer potential were on the increase due to intercalation in LDH nanocomposite, it was achieved alongside decreasing unwanted anti-cancer side effect on normal cells [41-43]. Most body organs, including the brain were accessible by LDH nanocomposite to deliver different types of drug, achievable, especially with those particles whose sizes are less than 250 nm [44], where specific area is the target for particular drug delivery coating with various agents are yielding amazing results [45-50].

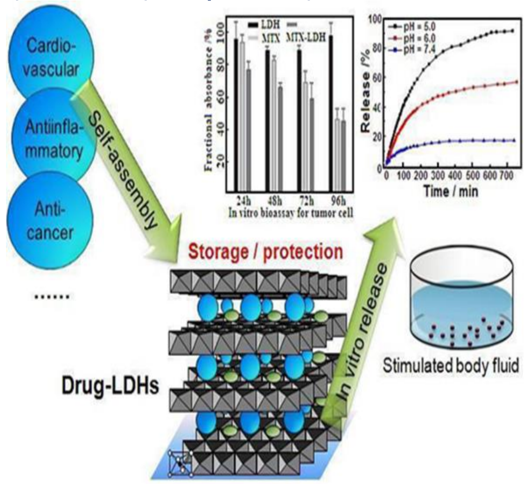

Fig. 12. Layered Double Hydroxide-Based Nanocarriers for Drug Delivery

Layered double hydroxide (LDH) nanoparticles have been studied as cellular delivery carriers for anionic anticancer agents. LDHs successfully accommodated intended drug molecules in their interlayer spacing. It was found that the anticancer efficacy of the intercalated drug was higher than other nanohybrids, free drugs, or their mixtures, which means the multidrug-incorporated LDH nanohybrids could be potential drug delivery carriers for efficient cancer treatment via combination therapy.

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