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Synthesising methods of layered double hydroxides and its use in the fabrication of dye Sensitised solar cell (DSSC): A short review

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Abstract. The layered double hydroxides (LDH) which are anionic clay substances comprising of stacked cationic layers and interlayer anions. The cationic sheets contain octahedral structure consisting the divalent and trivalent ions in the center and hydroxyl bunches in the corners, gathered by three bonding with the neighbouring octahedra on every side of the layer. The ratio between the quantity of cations and OH^- ions is 2:1, so a positive charge shows up on the layer because of the presence of trivalent cations. The interlayer space gives the compensation anions and water molecules, assuring a balanced out layered structure. The LDH materials were successfully synthesised from magnesium, aluminium, zinc and chromium chloride salts utilizing the co-precipitation technique. A Zn-Al LDH was researched as a potential sorbent material. This article reviews the recent advances in the preparation and intercalation of layered double hydroxides and its application in the fabrication of Dye Sensitized Solar Cell (DSSC).

1. Introduction

Layered double hydroxides (LDHs), named hydrotalcite-like materials, are anionic clay materials. In this review, we discuss about the various synthesising procedure of LDHs and its application in the fabrication of DSSCs [1]. LDHs depend on the complex layered structure as shown in Figure1. They are synthesised using numerous mixes of trivalent and divalent cations including aluminium, magnesium, nickel, zinc, chromium, iron, indium, copper, calcium and gallium [2]. Layered double hydroxides can be denoted by the formula:

$$[\mathbf{M}_{1-x}^{2+}\mathbf{M}_{x}^{3+}(\mathbf{OH})_2]^{x+}[\mathbf{A}^{n-}]_{x/n}\cdot m\mathbf{H}_2\mathbf{O}$$

where $\mathbf{M}^{3+}$ and $\mathbf{M}^{2+}$ are the trivalent and divalent layer cations separately, $\mathbf{A}^{n-}$ is the interlayer charge balancing anion, $\boldsymbol{m}$ is the number of water molecules, $\boldsymbol{n}$ is the charge, and $\boldsymbol{x}$ is the M^{3+} molar fraction. The material contains a positive charge that is adjusted by anions which are also pulled in to the surface or inserted into the layers. The structure provides LDHs standard anion properties which makes them novel among the clay materials, a large portion among them show deposits of cation properties [3].

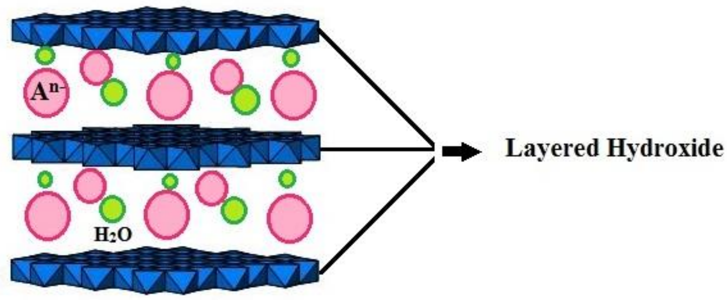

Figure 1. Structure of LDH

2. Preparation of Layered Double Hydroxides (LDHs)

A few techniques was shaped for the preparation of LDHs. This incorporate the urea technique, co-precipitation, ion exchange process and microwave light technique. Every synthesising methods have its own particular novel advantages and limitations when compared with alternate techniques [4]. The co-precipitation technique is the easiest and most regularly utilized of all techniques for the synthesis of LDHs. This technique includes the planning of two arrangements, the primary comprising the required metallic cations for example salts (ordinarily of nitrate or chloride) disintegrated the arrangement in their needed stoichiometric proportion. The other arrangement is an acidic arrangement at pH of range 4-5 or more noteworthy [5]. These metal cations will co-accelerate then the arrangement achieves super immersion. Unfortunately, LDHs arranged by co-precipitation frequently experience the bad effects of reduced crystallinity and nearness of pollutions. Conversely a technique similar to the urea method (that is from numerous points of view like co-precipitation) permits enhanced control of higher crystallinity and molecule size. In any case, the urea process is appropriate for planning of LDHs through high charge thickness, which means it can't be utilized to get ready LDHs comprising Cu^{2+} or Cr^{3+} [6].

3. Synthesising Methods of Layered Double Hydroxides (LDHs)

3.1 Urea process

The urea process is the process which takes an aqueous solution of urea and another solution of required metal salts were added and heated. After these reaction, urea hydrolyses in the solution, producing carbonate and ammonia ions into the solution [7]. This reasons due to pH of the solution which is regularly increase to pH 9, at which metal hydroxides precipitation occurs; or layered double hydroxides produces when more than one metal salt is present. Carbonate is the only interlayer anion utilizing these urea technique [8].

3.2 Co-precipitation Method

Typically, a blended solution of two different metal salts in distilled water is added drop wise over hours to an aqueous solution contains organic particles under nitrogen atmosphere with vigorous mixing. During titration, arrangement pH (7-8) is balanced with 0.1 N NaOH to accelerate co-precipitation reaction. Then precipitate, aged at room temperature for 24 hour, is centrifuged out, washed with distilled water completely and finally dried under vacuum as shown in Figure2. Biomolecules LDH hybrids can be set up by ion exchanging interlayer anion of LDH with biomolecules [9]. An aqueous mixed metal salt solution (anionic solution) and alkaline solution (cationic solution) are blended and aged to synthesis the Layered Double Hydroxide.

The interlayer anion which have selected (instead of urea process), and also be available in solution. The affinity of the anion which is important to remember (as specified already) to guarantee the sought interlayer anion winds up in the structure of LDH. The size of the particle can be altered by length of ageing period and the ageing temperature. Particle size can be reduced due to Minor ageing [7].The size is not commonly similar, as the materials in which shape first have a more extended time to growup [10].

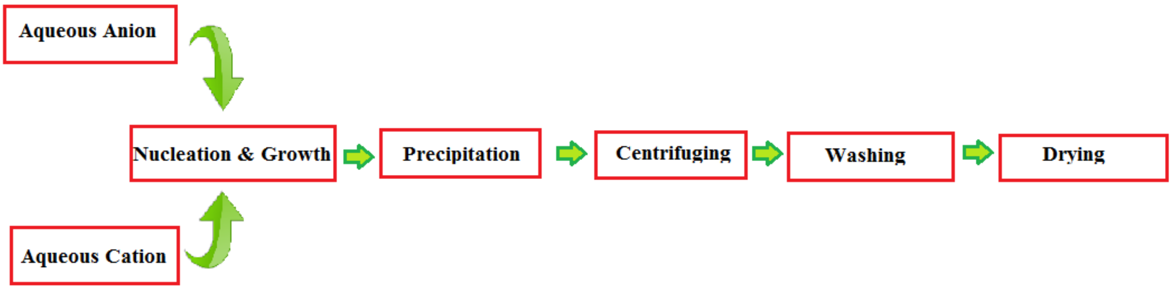

Figure 2. Flowchart of Experimental Procedure

3.3 Synthesis using Micro-wave

LDH synthesis using microwave is the point at which the ageing process of the interaction taking place in a microwave. The irradiation of microwave takes into consideration a quick ageing procedure, that is more often than not about 15-60 min [11]. The co-precipitation and urea techniques can be utilised as a part of a synthesis using microwave [12] , with the ageing using microwave rather than a reflux aging process. Homogeneous sized particles can be synthesised using microwave aging process, that is small size than particles produced using reflux aging method and frequently specific surface area has high [13].The advantage of shorter aging process is to prevent the formation of impurities while in the case of long aging process chance of the formation of impurities is high.

3.4 Ion-exchange process

The ion exchange process is utilized when the preferred interlayer anions which are most certainly not ready to be synthesised using urea or co-precipitation methods. The preferred anion replaces the anions existing in a formerly arranged layer double hydroxide. Nitrate and Chloride anions are regularly utilized as a part of the synthesised layered double hydroxides as they can be effectively changed with an extensive variety of natural and inorganic anions [7].

3.5 Reconstruction Method

Metal salts are calcinated at 500°C for 4 hour in nitrogen atmosphere at a heating rate of 5°C/min. This solid is then added to solution containing distilled water with guest molecule. pH (7-8) is adjusted by NaOH. Then, precipitate aged at room temperature, filtered, washed thoroughly with double distilled water and then finally dried under vacuum [14].

4. Characterisation Techniques Used For LDHs

Numerous systems are utilized to describe LDH and measure the adequacy as anion adsorbent. The techniques often include Near infrared spectroscopy (NIR), Powder X-ray diffraction (powder XRD), Energy-Dispersive X-ray spectroscopy (EDX), Infrared spectroscopy(IR), Raman spectroscopy and thermal investigation methods such as: Differential Thermal Analysis (DTA), Thermogravametric analysis (TGA), nitrogen BET surface range and Differential Scanning Calorimetry (DSC). Tests were described utilizing Thermogravametric Analysis (TGA) and powder X-ray diffraction (XRD) and to affirm the nearness of Layered Double Hydroxide [3]. XRD uncovered a trademark structure of LDH for all LDH tests. Thermal analysis experiments were employed to characterise the thermal stability of LDH with respect to weight loss of material. Preparatory tests for the evacuation of nitrate,sulphate and fluoride by a Mg-Al LDH were done, and the items were described utilizing TGA and XRD which demonstrated that a material used for LDH like the first hydrotalcite were framed after reconstruction. A Zn-Al LDH was researched as an adsorbent material for the removal of iodide and iodine from water. Researchers was found that LDH can be used as a good adsorbent material which can expel the greater part of the iodine present in the test arrangements [4]. Once more, the items were portrayed by Evolved Gas Mass Spectrometry (EGMS), TGA and XRD trying to get it the removal of iodine. XRD analysis indicated effective reorganization of the structure of LDH where TGA and EGMS demonstrated that lone a little measure of iodine components were lost amid warm disintegration.

5. Introduction To DSSC

Sunlight gives a clean, renewable and low cost energy source for individuals, while additionally serving as a primary energy source for another kind of energy sources, for example, water, bio-energy, wind energy and fossil fuel. The utilization of fossil fuels has added to the late increment in the greenhouse gas effect and CO_2 emissions, and also an unnatural weather change [15]. One approach to overcome these issues is by presenting a few types of renewable energy. The most available renewable energy source is solar radiation, which gives high temperature heat that can power a mechanical engine by changing over the radiation into a mechanical power and electricity to drive a generator or a machine. Solar energy can directly be changed over into electric energy using photo-voltaic (PV) effect [16]. Single-junction solar cells as well as single and multi-junction silicon solar cells are the original innovation of PVs. Second-generation PV cells introduces a thin film with lessen the constructional expense. The present third generation PV techniques in corporate double junctions, triple junctions and application of nanotechnology comes into solar cell fabrication [17]. Dye Sensitized solar cell is a third generation solar cell which gives a low cost technique to convert sunlight into electric energy. It is also called a photo electro chemical cell or photo active electrode based into a Nano structured metal-oxide film, such as TiO_2, ZnO, SnO_2, Nb_2O_5, $SrTiO_3$, CdSe,CdS,Fe_2O_3 etc. [18,19]. DSSC was invented by O'Regan and Gratzel in 1991by executing a TiO_2 Nano crystalline material as photo anode. In generally DSSC comprise of five principle components as shown in Figure3. (1) a glass substance of transparent conductive oxides (TCO); (2) a mesoporous semiconductor metal-oxide layer;(3)a single layer of organic or synthetic dyes attached to the surface of the Nano crystalline film; (4) a liquid electrolyte containing a redox couple iodide that interpenetrates the dye coated nanoparticles and(5) a platinum counter electrode [20,21].

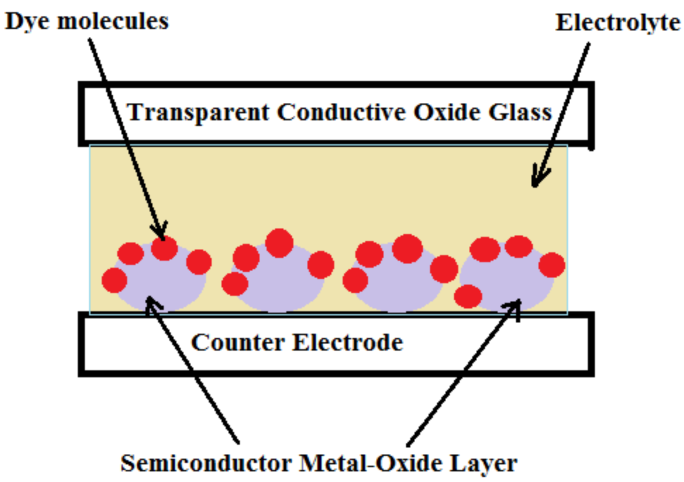

Figure 3. Structure of DSSC

6. Use of LDH as a Photoanode In Dye Sensitized Solar Cell

LDHs are formed having large specific surface area by using thermal treatment methods because of the breakdown of the layered structure of LDH and converted as Mixed metal oxides (MMO). The MMO has gathered interests as a capable photo catalyst for the conversion of solar energy and it additionally demonstrates the applications used in lithium batteries because of its specific surface area is high. Using conventional synthesising procedure for the production of LDHs, finely distributed metal oxides can be achieved from the LDH using calcination due to the constant dispersion of cations into layers of LDH [22]. The Mixed metal oxides is deliberated as a good material used for electrode to assemble the dye-sensitized solar cell (DSSC) since it is having same photoresponse, injection efficacy and band gap energy of TiO_2 and ZnO. The MMO possess extraordinary potential in assembling on a large scale production because of its cost is low, purity is high and quality control is good[23]. The efficiency of that assembled DSSC is depending upon the factors such as the ratio of $ZnAl_2O_4$ in the mixed metal oxides, calcined temperature and homogeneity of the film. Despite the fact that the Mixed metal oxide used Zn-Al LDH can keep up the layered structure, its moderately huge particle size when related with TiO_2 particles considerably decreases the adsorption capacity of Zn-Al MMO which reduces the efficiency of the assembled DSSC [24].

7. LDHs as an Additive in Polymer Gelled Electrolyte in DSSCs

One of the primary issues yet to be completely solved using liquid electrolytes in DSSCs is the volatility, spillage, and poor long term stability. Major research efforts have been committed to the improvement of gel or solid electrolytes to handle the issue. Moreover, the existence of liquid type electrolytes postured contests in trouble in actualizing tandem structures, incorporation of large area modules, conceivable desorption and photo degradation onto dye particles in the assembled DSSC, counter electrode corrosion and photo degradation of a few parts which lead to performance, lower lifetimes and practical use of the PV cells [25,26]. To withstand these issue, electrolyte combined polymer with provide substitute material which can be used in DSSC gadgets. In any case, lower ionic conductivity is the disadvantage of polymer type electrolyte when compared to liquid electrolyte. So, the efficiency of solar PV gadgets using electrolyte combined with polymer is lesser than the PV cells using liquid type electrolyte. As of now, gel type polymer electrolyte exchanged solid polymer electrolyte because of its ionic conductivity was greater than its solid condition, with a specific goal to enhance the performance of DSSC [27,28]. One of the principle issues for the advancement of gel or solid electrolytes is to diminish the drop in the power conversion efficiency achieved by the decreased ionic mobility in gel or solid electrolytes. Poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) gelled electrolytes with mica nanoparticles as the addictive substance to lessen the crystallinity of the polymer, prompting a higher PCE from 3.5 to 5.7% [29,30]. LDHs, as a type of anionic clay materials, were produced as the addictive for PVDF-HFP gelled electrolytes. PVDF-HFP is photo chemically stable and contains fluoride particles of high electronegativity that can facilitate well with Li+ to build the solubility of LiI in the electrolyte. Carbonate and chloride intercalated Zn-Al LDHs, $ZnAl\text{-}CO_3$ LDH, and ZnAl-Cl LDH can be also use [31].

8. Effect of LDH on the Photocatalytic Activity

Several biological dyes are mainly using in various industries like leather, cosmetics, paper and textile industries. The wastes generated from those industries, particularly textile industries includes a huge amount of toxic substances and dyes which are adding throughout the colouring procedure. They are hard to eliminate from various water treatment processes and be able to disposed through rivers and sewers easily. They might also endure degradation to produce extremely carcinogenic and toxic substances [5,32] .That's why there is an urgent need to develop an economic and efficient treatment method which are adept of deals through huge amount of polluted waters including significant amount of organic dyes.

So many techniques were described for the elimination of toxic dyes from polluted water, comprising sedimentation, flocculation, coagulation, adsorption, photodegradation, etc. [33,34]. The photocatalytic method gives substantial consideration via scientific peoples and also environmentalists because of the opportunity, by means of solar light that is free of cost besides renewable energy source.

Layered double hydroxides (LDHs) have been concentrated as of late, all things considered, as environmental-friendly materials that can be utilized as photo catalysts or photocatalyst supports. The researchers found that was one of the first to report the high photocatalytic activity of the ZnCr-LDHs, which energized future research in LDH materials as photocatalysts, considering that the utilization of LDHs as photocatalysts has for the most part been ignored up till then [35,36]. LDH found an expanding interest for the most recent couple of centuries and generally connected to the area of photocatalysis on account of their constancy, simplicity of planning and reduced cost. Besides, LDH can be synthesised with an assortment of trivalent and divalent cations and in this way, semiconductor constituents can be acquired by picking a appropriate chemical configuration. These were utilized for the photodegradation of various molecules, for example, phenolic mixes, pesticides, anionic dyes and cationic dyes [37].

9. Conclusion

LDH is entirely encouraging in different divisions of materials science. Essential advancement have been accomplished in the improvement of innovative sorts of LDHs aimed at present and unique applications like in dye adsorption and in the fabrication of DSSC. LDH can be used as a Photoanode as well as an addictive material in polymer gelled electrolyte in DSSCs. The Mixed Metal Oxides synthesised using ZnAl-LDH have the progressive aspect since the process is very easy to handle and the cost of the material is comparatively lower. Vitamin C anions could be interposed effectively in the interlayer structure of Zn-Al LDH, that have no influence on the hydroxide lattice of LDHs. In any case, additional studies to grow more reasonably for large scale manufacturing especially in full-sized anion trade applications and can enhance specific retention possessions of multi-anionic frameworks remain still mandatory. Parallel to the advances in nanoscience, a wide range of morphological types of nanopowders LDHs, circles, belts, fibrous structures, films, and so forth has been set up in the previous couple of centuries. Auxiliary and tunability of LDHs offers extensive usage as multifunctional resources for forthcoming applications in biomedicine and materials science.

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