Transition metal based layered double hydroxides tailored for energy conversion and storage

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Layered double hydroxides (LDHs) are a class of clays with brucite like layers and intercalated anions. The first (3d) series transition metals based LDHs (TM-LDHs) are attracting increasing interest in the field of energy conversion and storage processes due to their unique physicochemical properties. In this article, we review recent developments in the synthesis and applications of TM-LDH in these areas including water splitting, CO_2 conversion, metal-air batteries and supercapacitors and the underlying mechanisms of these processes. In addition, current challenges and possible strategies are discussed from the viewpoint of material design and performance.

Introduction

Layered double hydroxides (LDHs) are a class of two-dimensional (2D) anionic clays made up of positively charged brucite-like host layers and exchangeable charge-balancing interlayer anions (Fig. 1a) that can be expressed as $[M^{2+}{}_{1-x}M^{3+}{}_{x}(OH)_2]_x{}^{+}(A^{n-})_{x/n}\cdot mH_2O$ [1–4]. A fraction of divalent metal ions (such as Mg^{2+}, Fe^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, or Zn^{2+}) coordinated octahedrally by hydroxyl groups in the brucite like layers are uniformly replaced by trivalent metals (such as Al^{3+}, Cr^{3+}, Ga^{3+}, Mn^{3+} or Fe^{3+}) with the molar ratio of $M^{3+}/(M^{3+} + M^{2+})$ (the value of x) normally between 0.2 and 0.4 [2]. The interlayer charge compensating anion A is normally $CO_3{}^{2-}$, which is known to have a very high affinity to the LDH layers [5] but can nevertheless be decarbonated [6–8] and exchanged with other inorganic (such as Cl^-, $SO_4{}^{2-}$, etc.) or organic anions (such as acetate, lactate, dodecyl sulfate, etc.) [5]. The layered structure and the flexibility of incorporating mixed valence transition metal ions into the LDH structure in different compositions open the enormous potential to design high-performance catalysts on the molecular and nanometer scales. Moreover, as another attractive feature, such LDH materials can be converted into the corresponding mixed metal oxides (MMOs) with a uniform M^{2+} and M^{3+} distribution and a high surface area after calcination treatment.

Great efforts have been spent to tailor the physical and chemical properties of LDHs by changing the nature of metal cations, the molar ratio of M^{2+}/M^{3+}, the type of interlayer anions and so on to fulfill specific requirements for practical applications of LDHs in various areas, such as catalysis [9], fire retardants [10,11], pharmaceuticals [12], photochemistry/electrochemistry [13–21] and many others [2,22]. In particular, with the improvement of synthetic methods for transition metals based LDHs (TM-LDHs) [5,23] that have intrinsic electrochemical activities, there has been recently a rapid growth in publications related to the understanding and applications of LDH based materials in energy conversion and storage processes. In this review article, we firstly summarize the methods for synthesizing LDH nanosheets and then focus on the latest development of TM-LDHs (the TMs in the TM-LDHs reviewed in this article are mostly the first series transition metals) based materials as electrochemical/photochemical catalysts for water splitting and carbon dioxide reduction, as electrode materials for supercapacitors and metal-air batteries. The recurrent challenge in this rapidly growing area is to increase the performance including both activity and stability of LDH materials. Therefore, the structure-performance and chemical composition-performance correlations are addressed, which shed light on ways to develop promising electrode materials and catalysts based on LDH complexes in the future. In the final section, current challenges and possible strategies are discussed from the viewpoint of material design and performance. It is hoped that this review will attract

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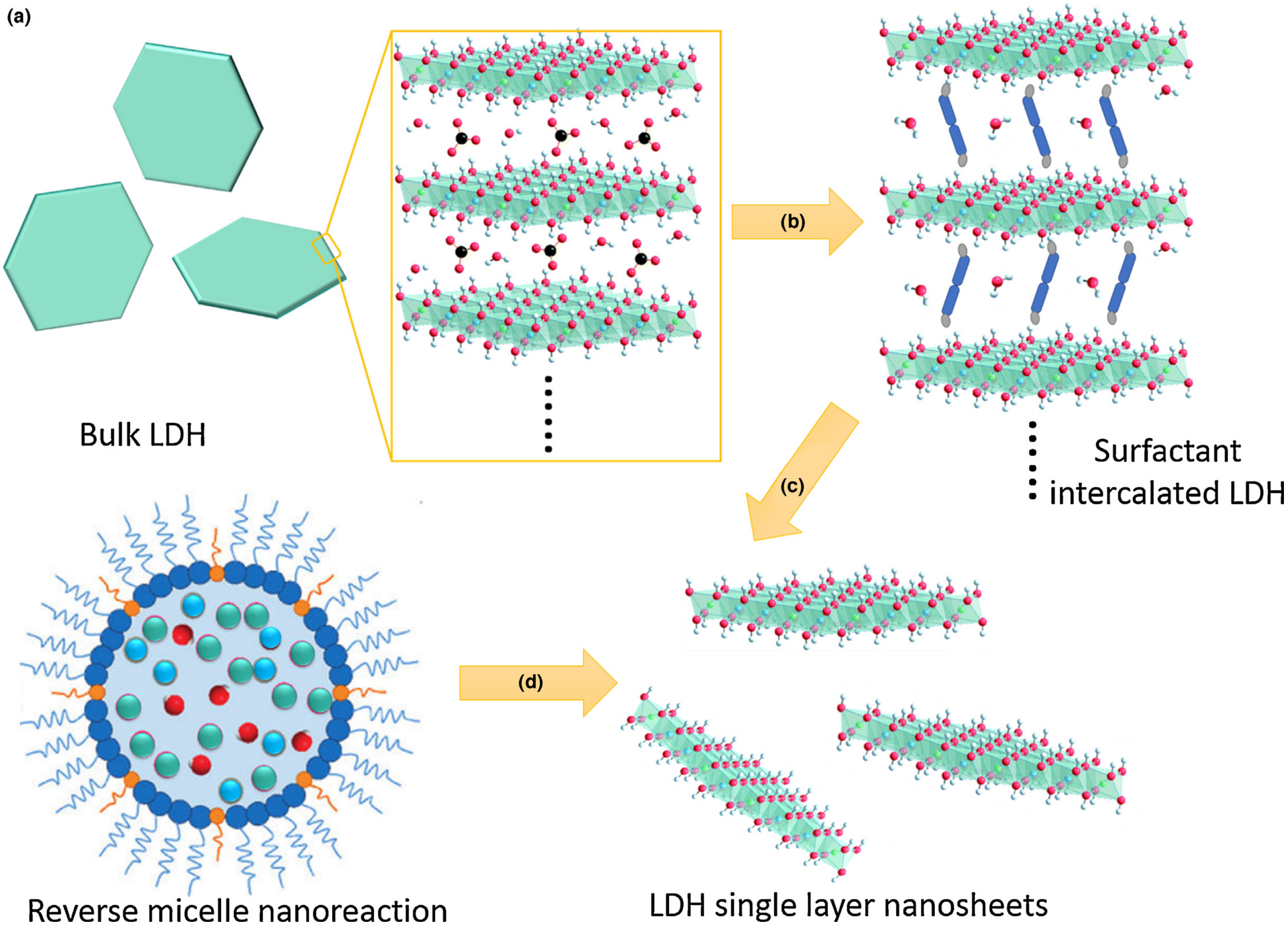

FIGURE 1

Schemes illustrating (a) the structure of carbonate-intercalated LDHs with the metal hydroxide octahedral layers stacked along the crystallographic *c*-axis, (b) the anion exchange process of LDH, (c) the delamination/exfoliation of LDH into single layer nanosheets, and (d) the bottom-up synthesis of LDH nanosheets in a reverse micelle.

more attention on LDH based nanomaterials and bring about further developments in this exciting area.

Synthesis of LDH nanosheets

Generally, LDH materials can be prepared by direct precipitation of mixed metal hydroxides in a solution. In theory, any divalent and trivalent metal ions with radii close to that of Mg^{2+} can constitute the host slabs of LDHs [24]. However, transition metals, especially Fe^{3+}, prone to form gel like hydroxides at low pH values [25,26], making it difficult to synthesize transition metal based LDHs by homogeneous precipitation. On the other hand, by using urea or hexamethylenetetramine as hydrolysis agents, highly crystallized TM-LDH microplates were hydrothermally synthesized in a recent study [23]. The crucial point here is the progressive hydrolysis of urea or hexamethylenetetramine that makes the solution alkaline and induces homogenous nucleation and crystallization of LDH materials. In addition to the hydrothermal method, Ma et al. synthesized a series of TM-LDHs with a highly crystalline hexagonal microplatelet structure through topo-chemical transformation. The advantage of this method lies in the rational control of the transition metal oxidation states in the hydroxide precursors [5,24]. Recently, a facile direct electrochemical deposition method and microwave assisted methods were also used to synthesize LDH based materials including NiCo [17,27], CoAl LDH [28,29], ZnCo LDH [30], etc., greatly broadening the landscape of LDH synthesis. In addition to the nanoparticle or nanoplate structures, LDH based core–shell [17,27,29], nanocone [30] and nanoflower [31] structures have also been reported. By studying the prototypes of ZnAl LDH and CoAl LDH, Forticaux et al. [31] recently found that the growth of LDH was driven by screw dislocations. By controlling and maintaining a low precursor supersaturation, LDH nanoplates with well-defined morphologies could be synthesized. In contrast, the uncontrolled overgrowth led to the LDH to develop a nanoflower morphology.

Research on the applications of LDH materials continues to expand crossing many disciplines, such as catalysts [3,20,32–36], catalyst precursors [32,37,38], anion exchangers [39], and electroactive/photoactive materials [2,15,18,35,36,40–56]. However, many of the applications are limited in scope because of the inaccessibility to the inner surfaces of the host layer. An effective solution to this problem would be to synthesize LDHs nanosheets with only a single highly anisotropic layer, which not only exhibit

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