



Review article

Exfoliation of layered double hydroxide solids into functional nanosheets

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ABSTRACT

Exfoliated layered double hydroxide (LDH) nanosheets are a class of positively charged 2D nanoparticles. These LDH nanosheets can be used for a wide range of functional polymer nanocomposites and hierarchically structured materials. In this review we summarize and evaluate latest scientific advances in exfoliating LDH compounds, including exfoliation methods, mechanisms, properties and applications of exfoliated LDH nanosheets. Then identify the prevailing challenges and the directions of future work. In the first section of this review we discuss the liquid exfoliation of LDH compounds, free of intercalation of organic species, in formamide, saturated aqueous L-asparagine or aqueous NaOH/urea solution with the help of ultrasonic treatment, mechanical shaking or stirring. We then examine the liquid exfoliation of LDH compounds with preceding organic species-intercalation. Such organic species include carboxylate, sulfonate, dodecyl sulfate, and amphoteric biomolecular amino acids. Next, we discuss the exfoliation of LDH in monomer or polymer to form LDH/polymer nanocomposites. The polymer nanocomposites include LDH/polyethylene, LDH/polyethylene-graft-maleic anhydride, LDH/poly (vinyl alcohol), LDH/polystyrene, LDH/poly (ethylene terephthalate), LDH/poly (butylene adipate-co-terephthalate), LDH/poly ((butylene succinate)-co-adipate), LDH/poly caprolactone, LDH/poly (L-lactic) acid, LDH/acrylic polymer, LDH/polyacrylamide, LDH/poly(amide-imide) and LDH/poly (methyl methacrylate). The properties of these LDH/polymer nanocomposites are also discussed. In addition to polymer nanocomposites, recent studies indicate that the exfoliated LDH nanosheets can be used in electrorheological media, magnetic materials, low infrared emissivity materials, catalysts, and biosensors. The literature survey and analysis suggests that future work should place emphasis on the innovation of green and cost-effective exfoliation methods, and deepen understanding of the interfacial interactions between the LDH nanosheets and organic species/polymers, and the new assembly tactics of exfoliated LDH nanosheets with functional molecules or nanomaterials to expand applications.

1. Introduction

Layered double hydroxide (LDH) compounds are a peculiar class of inorganic layered solids. The structure of LDH is commonly described in a general formula $[M_1^{2+}_{1-x}M_2^{3+}_x(OH)_2]^{x+}(A^{n-})_x \cdot nH_2O$, where $[M_1^{2+}_{1-x}M_2^{3+}_x(OH)_2]^{x+}$ indicates that each layer consists of a brucite-like ($Mg(OH)_2$) structure while carrying a net positive charge ($x+$) due to the partial substitution of trivalent metal cations (M_2^{3+}) for divalent metal (M_1^{2+}) cations (Fig. 1A, B). x (0.17–0.33) is the mole ratio of $M_2^{3+}/(M_1^{2+} + M_2^{3+})$ (Mills et al., 2012). The layer charge of LDH compounds is governed by the ratio of M_1^{2+} to M_2^{3+} and usually ranges from 200 to 400 $qe/\text{\AA}^2$ (Jobbágy and Iyi, 2010; Ma and Sasaki,

2010); the positive charges on the layer are balanced by interlayer anions (A^{n-}) (Kim et al., 2005; Nicotera et al., 2015), which are bound with positively charged layers by electrostatic force and are exchangeable (Meyn et al., 1990; Constantino and Pinnavaia, 1995). Water molecules (nH_2O) in the interlayer space have interactions with both the hydroxide layers and interlayer anions via hydrogen bonding (Fig. 1C) (Miyata, 1983; Cavani et al., 1992).

In view of the layered structure, charged layers and exchangeable interlayer anions, LDH compounds appear similar to layered silicate-based clay minerals although the elemental components are different. In this context, LDH compounds are often referred to as ‘anionic clays’ (Mills et al., 2012; Bergaya and Lagaly, 2013). In addition, LDH

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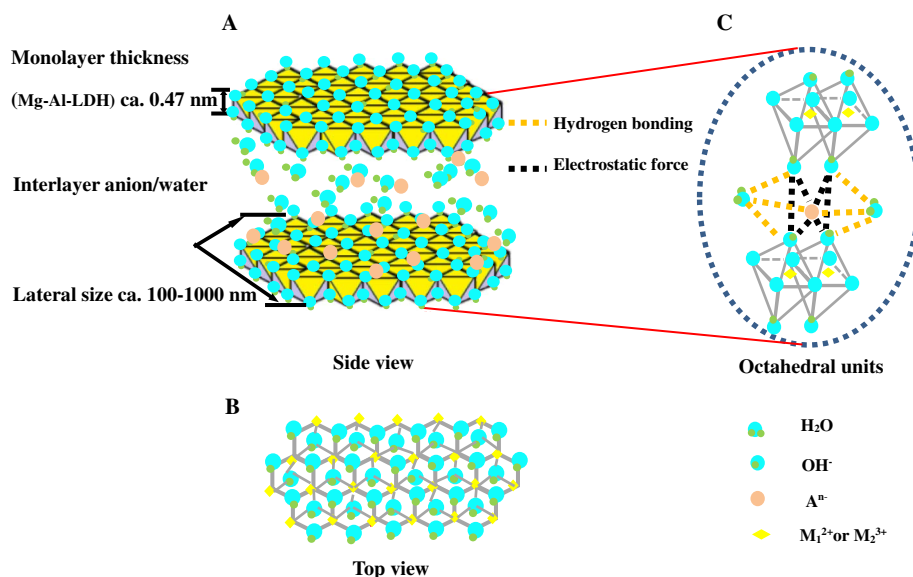


Fig. 1. Schematic drawing of the structure of LDH compounds. (A) Side view. (B) Top view. (C) Octahedral units of LDH compounds assembled through the hydrogen bonding of water molecules, electrostatic force of anions between the interlayer and hydroxyl group of the sheets. M_1^{2+} : Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} or Ga^{2+} . M_2^{3+} : Al^{3+} , Cr^{3+} , Mn^{3+} , Fe^{3+} , Co^{3+} , Ni^{3+} or La^{3+} . A^{n-} : OH^- , NO_3^- , Cl^- , ClO_4^- , CO_3^{2-} or SO_4^{2-} .

compounds appear analogous to naturally occurring hydroxylated minerals and are thus occasionally also termed ‘hydroxylated-like compounds’ sometimes (Feitknecht, 1942; Feitknecht and Gerber, 1942). Compared with their natural mineral counterparts, the composition of synthetic LDH compounds varies greatly (Fig. 1). The divalent metal cations (M_1^{2+}) can be Mg^{2+} , Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} or Ga^{2+} ; the metal trivalent cations (M_2^{3+}) can be Al^{3+} , Cr^{3+} , Mn^{3+} , Fe^{3+} , Co^{3+} , Ni^{3+} or La^{3+} ; the interlayer anions (A^{n-}) can be OH^- , NO_3^- , Cl^- , ClO_4^- , CO_3^{2-} , SO_4^{2-} or organic anions (Miyata, 1983; Cavani et al., 1992). The layered structure with exchangeable interlayer anions A^{n-} marks LDH compounds as unique materials for intercalation chemistry (Feitknecht, 1942; Feitknecht and Gerber, 1942). Studies have clearly indicated that a wide variety of species ranging from simple inorganic anions, through organic anions to complex biomolecules, can be intercalated into the interlayer space of LDH compounds by various strategies including ion-exchange, coprecipitation, dehydration-rehydration, also known as the reconstruction method, in situ polymerization, or exfoliation and re-assembly (Khan and O’Hare, 2003). Moreover, certain LDH compounds exhibit a property of shape selective intercalation (Khan and O’Hare, 2003). Intercalated LDH can be used as electronic, optical and magnetic materials (Zhang et al., 2005; Wang et al., 2010a, 2010b; Shao et al., 2012), adsorbents (Ma et al., 2016), catalysts (Silva et al., 2009; Zhou and Keeling, 2013; Zhou et al., 2016), biosensors (Shan et al., 2003; Zhou et al., 2011), drug vehicles (Lv et al., 2015) or directly as ion exchange hosts (Millange et al., 2000), fire retardant additives (Nyambo et al., 2008), and as cement additives (Leroux et al., 2001; Wang et al., 2014a).

While the knowledge on the intercalation of LDH compounds is continuously expanding, the last decade has witnessed an upsurge of studies on the exfoliation chemistry of LDH compounds. The exfoliation of LDH compounds refers to the process to swell and delaminate bulky LDH particles or crystals to yield separated nanosheets (Nicolosi et al., 2013). Ideally, a nanosheet is a single monolayer, which is ca. 0.47 nm (Mg-Al-LDH monolayer) in thickness and ca. 100–1000 nm in lateral size (Xu et al., 2013a) (Fig. 1).

Compared to a bulky LDH solid, exfoliated LDH nanosheets and 2D nanoparticles exhibit unique mechanical, thermal, electrical, magnetic, chemical, optical, and biological properties, explaining the upsurge in studies in recent years. Accordingly, there is great expectation that exfoliated LDH nanosheets will have significant potential in a wide

range of functional nanomaterials. In particular, exfoliated LDH nanosheets can be added into the matrix of polymers to form functional LDH/polymer nanocomposites.

Significant progress has been made in exfoliation of LDH compounds. Meanwhile, many applications of exfoliated LDH nanosheets have been explored, covering physical, electrochemical, magnetic, catalytic and optical areas. This review aims to summarize and examine the technological progress and scientific understanding of the exfoliation of LDH compounds, followed by a discussion on the potential of exfoliated LDH nanosheets and the existing problems and challenges.

2. Direct exfoliation of LDH in formamide, aqueous L-asparagine or NaOH/urea solution

Although LDH compounds contain exchangeable anions, due to the high charge density, their swellability in water is much poorer than smectitic clay minerals. Hence, to exfoliate bulky LDH crystalline particles directly in water appeared difficult (Adachi-Pagano et al., 2000; Jobbágy and Iyi, 2010; Ma and Sasaki, 2010; Wang and O’Hare, 2012). However, a few recent studies have shown that exfoliation of LDH compounds can be directly achieved by the judicious selection of solvents (Leroux et al., 2001; Zhang et al., 2015) with the aid of ultrasonic treatment, mechanical shaking or stirring. For example, formamide ($HCONH_2$) (Wu et al., 2005; Li et al., 2005; Ma et al., 2006; Abellan et al., 2010; Zhang et al., 2015; Liu et al., 2016) (Fig. 2). Formamide is highly polar (polarity index: 7.3 (Snyder)). Its carbonyl group ($C=O$) at one end has strong interactions with the LDH layers, the interlayer water molecules and anions, while its $-NH_2$ group at the other end has poor interactions with the LDH layers, the interlayer water molecules and anions (Ma et al., 2006). As a result, the replacement of interlayer water with formamide will disrupt the original strong hydrogen-bonding network, weaken the interlayer attraction force and then facilitate exfoliation. Nevertheless, even in formamide, external force via ultrasonic treatment and mechanical stirring is still imperative to exfoliate LDH. Under ultrasonic treatment, acoustic cavitation of high frequency ultrasound (20–130 kHz) leads to the formation, growth and collapse of microbubbles in solvents and induces shock waves and a microjet flow on the external surface and interlayer space of the LDH, thereby weakening the interlayer interaction (Wu et al., 2005; San Roman et al., 2008), delaminating the layered crystallites and producing exfoliated nanosheets. For example, Wu et al.

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