

A facile approach for synthesizing Fe-based layered double hydroxides with high purity and its exfoliation

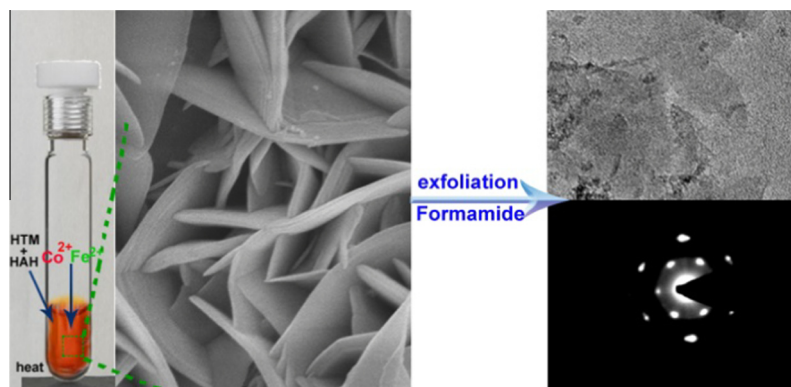


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GRAPHICAL ABSTRACT

A facile approach has been developed for synthesis of Co-Fe LDH with high crystallinity, using hydroxylamine hydrochloride as reducing and complexing reagent without piping N_2 to the system.



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ABSTRACT

Transition metal (e.g., Fe, Co, Ni)-based layered double hydroxides (LDHs) and their exfoliated nanosheets have great potential applications due to their redox and magnetic properties. Here we report a facile approach for the preparation of Co-Fe LDHs with good crystallinity and high purity. The proposed approach includes two steps: (1) The mixed divalent metal (e.g., Co^{2+} , Fe^{2+}) hydroxides were first synthesized using a homogeneous precipitation without piping N_2 into the system; hexamethylenetetramine (HMT) was the hydrolysis agent providing OH^- , and hydroxylamine hydrochloride (HAH) was used as both a reducing and a complexing reagent. (2) Then the as-prepared hydroxides were slowly oxidated by air and simultaneously intercalated by CO_3^{2-} to form CO_3 -intercalated LDHs. The Co-Fe LDHs were roundly characterized by XRD, SEM, EDX and FT-IR. The effect of HAH on the morphology and structure of the Co-Fe LDHs was also studied. The magnetism of Co-Fe LDHs at room temperature was investigated and the results showed that the LDHs displayed a low saturation magnetization value of 6.3 emu g^{-1} , suggesting that the purity of the products was very high. In addition, the intercalated CO_3^{2-} in the Co-Fe LDHs could be successfully exchanged with other anions such as Cl^- and ClO_4^- . Furthermore, the exchanged-LDHs could be exfoliated in formamide. This work establishes a new method for the synthesis of Fe-based LDHs with good crystallinity and high purity under mild conditions, and can accelerate the development of applications using these layered materials.

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1. Introduction

Layered double hydroxides (LDHs), also known as hydrotalcite-like compounds or anionic clays, are a type of inorganic layered material, which structurally consist of positively charged brucite-type octahedral layers with charge compensated anions and water molecules occupying the interlayer spaces [1–6]. Increasing attention has been paid to these synthesized 3D layered materials due to their potential for use in a wide applications [7–17]. However, compared with 3D LDHs, the 2D nanosheets of LDHs have many advantages. For example, they have an increased surface area which is beneficial to surface activity or catalytic activity [18–21]. At the same time, the nanosheets also possess a modified electronic band structure that makes them display unique optical and electrical properties. Moreover, these 2D nanosheets can be assembled to form functional films or can serve as the building blocks of other multifunctional materials. The first delamination of LDHs was realized by dispersing dodecyl sulfate intercalated Zn–Al LDHs in butanol in 2000 [22]. Since then, Al-based LDHs have been exfoliated into positively charged nanosheets using different methods. The exfoliated nanosheets could then be assembled with a wide variety of negatively charged functional materials, where the composites display the desirable properties [23–26]. Fe-based LDHs have great potential for applications involving electrochemical biosensors and electrocatalysts. For example, Mg–Fe LDHs have been used to immobilize heme proteins for the sensing of H_2O_2 [8]. Co–Fe LDHs supported on graphene have been used as a precursor to prepare efficient Pt-free electrocatalysts for the oxygen reduction reaction (ORR) [27]. Ni–Fe LDHs have been studied intensively as an electrocatalyst for the oxygen evolution reaction (OER) [28–33]. Recently, it was reported that the exfoliated single-layer nanosheets of Ni–Fe LDHs exhibited a significantly higher OER activity than the corresponding bulk LDHs [34]. Therefore, it is significant to synthesize via exfoliation 2D Fe-based LDH nanosheets with high crystallinity and a regular shape.

Although homogeneous precipitation using urea or hexamethylenetetramine hydrolysis is successful for preparing Al-based LDHs with good crystallinity [35], it is not applicable to Fe-based LDHs because the Fe^{3+} ion lacks the desirable amphotericism like that of the Al^{3+} ion. Thus, various novel strategies have been employed for the synthesis of Fe^{3+} -based LDHs with high crystallinity [36–41]. Among these strategies, the method using additional chelating reagents [37,38] and the topochemical approach developed by Sasaki and coworkers [36] are effective and remarkable. In the so-called topochemical approach, brucite-like Co^{2+} – Fe^{2+} hydroxides are first prepared by a homogeneous precipitation, and then they are oxidized by iodine (I_2) in chloroform (CHCl_3) and intercalated by I^- . The Co–Fe LDHs synthesized by this method exhibit good crystallinity and perfect hexagonal shapes and can be exfoliated into nanosheets. However, except for Sasaki and coworkers, this method has seldom been adopted for the synthesis of Fe-based LDHs [36,42–44]. We think that this method is difficult for other researchers to follow because of the strict experimental conditions. To carry out this topochemical approach, nitrogen gas (N_2) should be purged during the full refluxing process to expel O_2 and the filtering of the Co^{2+} – Fe^{2+} hydroxides should be performed in a glove bag filled with N_2 . In fact, all of the experiments including synthesis and characterizations must be performed with absolutely no O_2 and CO_2 [36]. In addition, the oxidative intercalation should be operated in an iodine/chloroform solution, which makes this method less green.

Here, we aim to improve the technology of this topochemical approach by two aspects to obtain the Fe-based LDHs with high quality more easily. First, during the process of synthesizing the Co^{2+} – Fe^{2+} hydroxides, a reducing agent with complexing effect

was added to replace N_2 protection, which not only prevented the oxidation of Fe^{2+} but also possibly improved the crystallinity of the Co^{2+} – Fe^{2+} hydroxides [37,38]. It should be noted that the intermediate, Co^{2+} – Fe^{2+} hydroxide, need not be separated from the reaction system, which makes the proposed method easier to perform. Hydroxylamine hydrochloride (HAH) is a strong reducing agent, especially in basic aqueous solution [41,45]. Moreover, HAH can complex with metal ions via a N atom and also has a low toxicity, which makes it an appropriate auxiliary reagent. Second, the as-prepared Co^{2+} – Fe^{2+} hydroxides were slowly oxidized by the air and intercalated by CO_3^{2-} simultaneously, which was proven by the literature [46]. The anion exchange and exfoliation of the Co–Fe LDHs prepared by this facile method were also investigated in detail.

2. Experimental

2.1. Chemicals

Hydroxylamine hydrochloride (HAH, $\geq 98\%$), $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ($\geq 99\%$), $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ($\geq 99\%$), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ($\geq 99\%$), hexamethylenetetramine (HMT, $\geq 97\%$) were obtained from J&K Scientific Ltd. (Shanghai, China). Other chemicals were of pure analytical grade and used without further purification. Milli-Q purified water (Millipore, Resistivity $\geq 18.2 \text{ M}\Omega \text{ cm}$ at 25°C) was used throughout the study.

2.2. Synthesis of Co–Fe LDHs

Co–Fe LDHs were prepared by first forming Co^{2+} – Fe^{2+} hydroxides via homogeneous coprecipitation and further oxidation by air.

Typically, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and HAH were dissolved in decarbonated water in a sealed tube. Then $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (the molar ratio of $\text{Co}^{2+}/\text{Fe}^{2+}$ is 2:1) was added into the above mixed solution. When the temperature of the mixture rose to 80°C (T_1), HMT was introduced into the solution as quickly as possible. The mixed solution was then refluxed at 110°C for 5 h under continuous magnetic stirring. The reaction equipment is shown in Fig. S1 (see Supplementary data). A very long sealed tube was used because it not only prevented the entry of air/ O_2 but also allowed the solution refluxing safely.

After the reaction was finished, the sealed tube was opened and the air was allowed to oxidate the as-prepared Co^{2+} – Fe^{2+} hydroxides. Then the resulting yellow solid product was centrifuged, and washed with pure water and anhydrous ethanol several times. Finally the product was dried at room temperature in a vacuum drying oven.

2.3. Synthesis of Ni–Fe LDHs and Mg–Fe LDHs

Ni–Fe LDHs and Mg–Fe LDHs were synthesized via the process similar to that of Co–Fe LDHs. It should be noted that the optimal conditions are different for the different LDHs and are listed in Table S1.

2.4. Anion exchange and exfoliation of Co–Fe LDH

The process of anion exchange and exfoliation of Co–Fe LDHs was similar to the literature [35]. However, the amount of reagents and the stirring method were adjusted according to practical conditions.

Typically, 30 mg Co–Fe LDHs was dispersed into 30 mL decarbonated water by ultrasonication for 20 min. Then, 1.755 g NaCl and 7.5 μL 3.0 M HCl were added to the suspension of Co–Fe LDHs and the suspension underwent another 20-min ultrasonic

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